Lawrence Berkeley National Laboratory

Recent Work

Title
PRODUCT MAGNETIC DEFLECTION SLOTTED DISK VELOCITY ANALYSIS MOLECULAR BEAMS KINETICS: LiO(X2 *1) and LiO(A2-) FROM Li + NOp

Permalink
https://escholarship.org/uc/item/14g097xq

Author
Sholeen, Charlotte M.

Publication Date
1976-03-01
PRODUCT MAGNETIC DEFLECTION SLOTTED DISK VELOCITY ANALYSIS MOLECULAR BEAMS KINETICS: LiO(X^2Π) AND LiO(A^2Σ) FROM Li + NO_2

Charlotte M. Sholeen and Ronald H. Herm

March 1976

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48

For Reference
Not to be taken from this room
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
PRODUCT MAGNETIC DEFLECTION SLOTTED DISK VELOCITY ANALYSIS MOLECULAR BEAMS KINETICS: LiO(\(X^2\Pi\)) AND LiO(\(A^2\Sigma\)) FROM Li + NO\(_2\)

Charlotte M. Sholeen\(^{2}\) and Ronald R. Herm

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley and

Ames Laboratory - ERDA and Department of Chemistry
Iowa State University, Ames, Iowa 50011*

ABSTRACT

Product magnetic deflection-slopped disk velocity analysis establishes both LiO(\(X^2\Pi\)) and LiO(\(A^2\Sigma\)) as products of the Li + NO\(_2\) bimolecular reaction. Velocity distributions of LiO(\(X^2\Pi\)) reactively scattered from crossed thermal beams of Li and NO\(_2\) are reported. Transformation of these data into the center-of-mass - coordinate system provides a contour map of the differential reactive cross section which indicates that: (a) the reaction mechanism is direct, i.e. the lifetime of the LiNO\(_2\) intermediate is less than its rotational period; (b) the LiO(\(X^2\Pi\)) product is preferentially scattered forward, i.e. in the direction defined by the Li velocity; (c) an appreciable fraction of the reaction exothermicity (\(\sim 45\%\)) appears as product recoil energy; and (d) distributions in product recoil angle and energy are weakly coupled with forward scattering favoring higher recoil energy.

\(^{2}\) Present address: Department of Physics, University of Edinburgh, Edinburgh, EH9 3JZ, Scotland

\(^{*}\) Correspondence should be addressed to RRH at this address.
Reaction kinetics involving gaseous alkali atoms continue to be studied extensively. Current work includes determination of absolute rate constants for ground $^1,^2$ and excited $^3$ states as well as crossed molecular beam determinations $^4$ of reaction dynamics of ground state species. Despite this continuing effort, relatively little work has appeared on reactions of Li, the simplest metallic atom. In the area of crossed beams studies, the technique of two filament differential surface ionization, which distinguishes reactive from non-reactive scattering in studies with the heavier alkali metals, is not applicable $^5$ to the study of Li atom reactions. In recent years, the replacement of the surface ionization detector by an electron bombardment (EB) ionizer-mass filter unit has vastly extended the chemical scope of the crossed beams technique into the non-alkali regime. The lithium halides have a lower probability of fragmentation upon EB ionization than do the halides of the heavier alkalis. $^6$ Nevertheless, EB ionization would be a questionable choice for a general detection technique for the study of Li atom reactions because of the high exothermicity of many of these reactions and the uncertain dependence of the EB fragmentation probability on internal excitation.

An earlier crossed beams study in our laboratory $^5$ determined product angular distributions from a number of Li atom reactions. In these studies, an inhomogeneous electromagnet placed between the crossed beams intersection region (BIR) and surface ionization detector deflected aside a known fraction of the non-reactively scattered Li atoms and made
possible a measurement of the reactive scattering intensity. This present series of papers represents an extension of these early "primitive" experiments by the incorporation of a slotted disk velocity analyzer (SDVA) immediately in front of the deflecting electromagnet. This paper, the first of the series, includes a discussion of the product magnetic deflection - SDVA experimental technique and reports results on the reaction of Li + NO₂. This reaction provides a particularly interesting application of the technique because the LiO product possesses an unpaired spin.

Throughout this series, results on a particular Li atom reaction will be discussed in relation to the analogous reactions of the heavier alkalis and, where appropriate, the hydrogen atom. The relatively limited number of published reports of laboratory (LAB) product velocity measurements and derived center-of-mass (CM) recoil distributions for alkali atom reactions are listed in Table I. Additional unpublished data of this sort has also been briefly described in the literature (e.g., Refs. 4c, 8 and 9). This table does not, of course, reference the many other types of measurements which have been reported for alkali atom reactions.

**APPARATUS AND EXPERIMENTAL CONDITIONS**

The apparatus is similar to that employed in Ref. 5 with the addition of the SDVA. It is described in detail in Ref. 10 and is shown schematically in Fig. 1. Pertinent dimensions are listed in Table II.

The product analysis section (A-K and X) was isolated by thick aluminum foil affixed to the analyzer shield (K) and pumped by a 6" oil DP. The rest of the assembly was pumped by another 6" DP and extensive LN₂ cold shielding not shown. Beam sources were not differentially pumped so that experiments were restricted to reactant gases condensible
on the LN$_2$ surfaces in order to maintain the ambient background pressure below 10$^{-6}$ torr.

The beam source assembly (M-W) could be rotated about the BIR so as to measure the scattered LAB angular distribution in the plane defined by the inserting beams between $\Theta = -15^\circ$ and $+100^\circ$. By convention, $\Theta = 0^\circ$ and $90^\circ$ are defined by the Li and gas beam directions, respectively. The Li$^+$ source (U) was a conventional stainless steel (SS) two-chamber oven equipped with knife-edge slits. Early experiments were plagued by the tendency of molten Li to leak out around the seal in the lower chamber. This problem was eliminated by compressing a nickel sealing gasket and testing that the resulting seal was vacuum tight prior to pump-down. Reactant gases were prepared at the desired pressure on an external gas line and emerged from a variable temperature, SS reservoir (N) through a many-channel array. This array was fabricated from a SS disk$^{11}$, 0.051 cm thick, containing 170,000 holes per cm$^2$ and a 32% open area. The cross beam typically attenuated the Li beam by $\sim 5\%$ under operating conditions. It was square-wave modulated, typically at 42 Hz, by means of a rotating cylinder (O); the reference signal for the lock-in amplifier was taken from the lamp-photo transistor assembly (G and R).

As in earlier studies$^5$, scattered Li atoms and LiX products were detected as Li$^+$ by surface ionization on a 1630°K oxygenated$^{12}$ tungsten ribbon (A) spring-mounted between focusing and accelerating grids shown in Fig. 1. The mass spectrometer electromagnet (C) was included to separate the Li$^+$ signal from the copious K$^+$ background always present in the surface ion spectrum. The mass spectral resolution was not quite sufficient to resolve $^6$Li and $^7$Li; nevertheless, all data were collected
at a setting which strongly favored detection of the $^7$Li isotope. The Li$^+$ desorption time reported$^{13}$ for an oxygenated tungsten surface at 1630 °K is too short to distort the 42 Hz modulation of the scattered signal. This was also verified experimentally by comparing scattered signals measured in AC and DC detection modes. The entire detector assembly (A, B, C, D, and X) in Fig. 1 could be moved right and left so as to measure displacement profiles (deflecting electromagnet (E) off) and deflection patterns (electromagnet magnet energized).

**Slotted Disk Velocity Analyzer**

Since the surface ionization response time would be too slow$^{13}$ to permit time-of-flight measurements of the LiX LAB velocity, an SDVA (J) was constructed from six Alcoa 2024-T3 aluminum alloy disk, 0.16 cm thick, arranged in an approximate geometric sequence according to the procedure described by Kinsey$^{14}$. Each disk contained 345 slots of average width 0.071 cm at an average radius of 7.3 cm. In view of the relatively high thermal speeds of Li atoms, the disk were aligned at a relatively small rotation angle, 2.54°, to produce an analyzer 6.55 cm long with a roughly triangular bandpass function, $B(v_o, v)$, centered on the nominal transmitted velocity, $v_o$, with a resolution of $\Delta v/v_o = 0.20$ (FWHM). This nominal transmitted velocity is proportional to $f$, the rotations per second of the shaft:

$$v_o = Rf.$$  \hspace{1cm} (1)
The selector was designed for a value of $R = 9.00$ m. A photodiode (I) monitored the waveform produced by the rotating slots passing a light bulb (G) in order to insure that the analyzer locked-in at the driving frequency.

The rotor shaft was turned by a dual-winding synchronous hysteresis motor positioned directly below the deflecting electromagnet, $E$. Initially, it proved impossible to lock-in the rotor at any reasonable frequency when this magnet was energized. Enclosing the analyzer motor in a series of three cylinders, the middle of brass and the inner and outer of cold-rolled steel, partially shielded the motor from this field. Nevertheless, the motor still required much higher power levels when the magnet was energized. This produced rapid heating in the motor which made it impractical to collect data for long periods of time with the magnet energized. This was inconsequential in studies of the scattered product intensity where the deflecting magnet was energized only briefly at a given angle-velocity setting. However, it rendered auxiliary measurements of the deflection patterns of paramagnetic species very troublesome. It also proved necessary to build a mu-metal box (X) around the Bendix Spiraltron model 306 electron multiplier (B) because its gain appeared to change somewhat when the deflecting field was energized in early experiments where $X$ had not been installed.

**Beam Speed Distributions**

Since this analyzer, unlike that described by Grosser$^{15}$, was designed to turn in only one direction, it was not self-calibrating. Since its absolute calibration, $R$ of Eq. (1), was dependent on the degree of alignment of the rotor shaft with the detector line-of-sight, it was necessary to calibrate against the known Maxwell-Boltzmann thermal speed distribution obtained
from the Li oven at very low source pressures. The procedure was to first position the Li oven properly by (1) positioning the surface ionization filament at the center of the displacement profile of a scattered signal and (2) subsequently rotating the oven assembly to center the Li beam. The Li beam speed distribution was then measured versus \( f \) at low Li source pressures and was least-squares fit to the known thermal distribution by convoluting over the analyzer bandpass function, \( B(v_0, v) \), while varying \( R \) of Eq. (1) as the parameter. Experimental values of \( R \) determined in this way which were used in actual data analysis were always within 5% of the design value. Typical data and fits are shown in Fig. 2. Throughout the paper, measured (and calculated) speed distributions which are presented have been corrected for the speed-dependent transmission of the SDVA by dividing the actual transmitted signal by \( v_0 \). In addition to calibrating the SDVA, the good fits of the data to thermal distribution functions, such as are shown in Fig. 2, also established negligible attenuation by the ambient background gas despite the long beam path length.

The LAB - CM transformation of reactive scattering data requires a knowledge of the beam speed distributions. This, of course, was routinely measured for the Li beam. As expected, the higher Li beam source pressures employed in the scattering measurements resulted in a relative attenuation of the lower speeds present in the thermal distribution. Since no theoretical expression adequately reproduces experimental speed distributions in this beam source region \(^{16}\), it proved convenient to fit the measurements to an empirical number density probability density speed distribution,

\[
p(v) = \rho_0 \left[ \frac{(v - u)^2}{\alpha^3} \right] \exp \left[ - \frac{(v - u)^2}{\alpha^2} \right] h(v - u).
\]

(2)
Here, \( p_0, u, \) and \( \alpha \) are adjustable parameters, and \( h(x) \) is the unit step function \([0 \text{ for } x < 0, \ 1 \text{ for } x > 0]\).

By reversing its potential, the tungsten ribbon became an electron emitter and the detector unit, A-D, served as a low resolution mass spectrometer detector for the cross beam. This was impractical for detecting some beams, such as \( \text{NO}_2 \), because of an intolerably high background mass signal due to some component of the ambient background pressure. For some heavier cross beam materials [\( \text{Cl}_2, \ 	ext{Br}_2, \ 	ext{PCl}_3, \) and \( \text{SnCl}_4 \)], however, this permitted measurements of the cross beam angular profile (Table II) and speed distribution. In agreement with observations reported in Ref. 17 on a "crinkly-foil" many-channel array, measured speed distributions were well fit by Eq. (2) with \( \alpha \) fixed at the most probable source speed, \( \alpha^2 \ = \ 2kT/m \). As in Ref. 17, \( u \) increased with increasing source pressure for fixed source temperature. Deviations from thermal behavior for this present source are less than those reported in Ref. 17 but still somewhat greater than those predicted in Ref. 18.

Fig. 3 shows data as well as fits to Eq. (2) calculated recognizing that the detector responds to number density rather than flux density in this mode. Beam speed distributions for gases not directly measured in this study (e.g., \( \text{NO}_2 \)) were estimated\(^{10}\) from the empirical correlations of Ref. 17 after scaling to those results which were measured here. This should be more than adequate since correction for the spread in the cross beam speed distribution represents only a second-order correction to the \( \text{LAB} - \text{CM} \) transformation of reactive scattering.

Viewing Factor Correction

The entries in Table II indicate that the detector sees only a \( \Theta \)-dependent fraction of the BIR through slits F and L. As a consequence,
all LAB scattered intensities reported in this series of papers have been multiplied by a viewing factor correction,

$$\beta(\theta) = \frac{\text{total scattering volume}}{\text{effective scattering volume viewed by detector}}.$$  \hspace{1cm} (3)

Ref. 5 points out that $\beta(\theta)$ cannot be calculated to sufficient accuracy from theoretical slit widths and distances because it is very sensitive to small misalignments ($\sim 0.05$ cm) of these slits with respect to lines-of-sight through the BIR. Fortunately, however, $\beta(\theta)$ is easily measured as

$$\beta(\theta) = \frac{\text{scattering measured with no detector collimation}}{\text{scattering measured with detector collimation}}.$$  \hspace{1cm} (3)

Thus, $\beta(\theta)$ can be evaluated from (a) the ratio of total scattered intensities or (b) the ratio of reactively scattered intensities. The numerators for Eq. (3) were taken as the angular distributions reported in Ref. 5 since small differences in beam angular and speed distributions between Ref. 5 and this present study should have negligible effect on the true angular distributions. The SDVA assembly in Fig. 1 (J, I, and G) could be lowered out of the detector viewing plane during an experiment, without disturbing the alignment of any other component, in order to measure the total scattered intensity with the detector collimation in place, i.e., the denominator for Eq. (3), ratio (a). In this manner, $\beta(\theta)$ was determined for each reaction included in this series from Eq. (3), ratio (a), except for Li + SnCl$_4$ where ratio (b) was employed because an experimental malfunction prevented determination of the denominator needed for ratio (a).

Three different types of checks were employed to verify the $\beta(\theta)$ functions used. For Li + NO$_2$, Cl$_2$, Br$_2$, and SnCl$_4$, $\beta(\theta)$ was also calculated from Eq. (3), ratio (b). In these calculations, the denominators
were evaluated by numerically integrating the measured LAB LiX product distributions over recoil speed at each $\Theta$; this required a slight extrapolation of the high speed tails for NO$_2$ and Cl$_2$. For Li + Cl$_2$, $\beta(\Theta)$ was also evaluated for $\Theta \geq 25^\circ$ from ratio (a) with a numerator measured in the present experiment. A weak tail on the Li beam profile, decreasing from $\sim 4\%$ to $\sim 0.08\%$ of peak intensity as $\Theta$ increased from $5^\circ$ to $20^\circ$, which was inconsequential to any other measurements reported here, precluded measurement of the numerator at smaller $\Theta$. There was considerable variation in qualitative shape of the $\beta(\Theta)$ functions from reaction to reaction. However, computer simulations$^{10}$ demonstrated that this range of $\beta(\Theta)$ shapes was consistent with estimated alignment precisions of the only apparatus parameters which might have varied from reaction to reaction, slits U and T. Finally, it should also be noted that $\beta(\Theta)$ never varied by more than a factor of five over the range of $\Theta$ values where reactive scattering data was collected.

Inhomogeneous Deflecting Magnet

The inhomogeneous deflecting electromagnet, shown in Fig. 4, was similar to that employed in Ref. 5. The pole tips (0.16 and 0.24 cm radii, 0.25 cm apart) were of the conventional "two-wire" design.$^{19}$ The magnet yoke, 11.4 cm long, was wound by 38 turns of water-cooled tubing. The field in the gap saturated at $\sim 3000$ amp-turns at an estimated field strength of $\sim 9kG$. All data on reactive scattering were collected at this "standard field" which is clearly in the high field limit where nuclear and electronic magnetic moments are decoupled so that only the latter need be considered in interpreting deflection patterns. Thus, the deflection of a particle of mass $m$ traversing the field at speed $v$ may be written$^{19}$

$$s(v) = K_g\mu_0 M_f/mv^2$$

(4)
in terms of the Bohr magneton and an apparatus constant $K$ to be determined. For Li, of course, $g_J = 2$ and $M_J = \pm 1/2$. It is interesting to note that this magnetic deflection-SDVA combination functions as a low resolution ESR spectrometer if $m$ is known or, alternatively, as a mass spectrometer for neutral species if $g_J$ is known.

Figure 4 illustrates the use of this field in measuring reactive scattering intensities for a case where it is known that $g_J = 0$ for the LiX product. The data shown were collected during a study of Li + Br$_2$. Panel (d) clearly shows the separation of non-reactively scattered paramagnetic Li atoms from reactively scattered diamagnetic LiBr molecules at an intermediate SDVA speed setting. Panels (c) and (e) indicate that the scattering is almost totally reactive at low recoil speeds, totally non-reactive at high recoil speeds. If the SDVA resolution were perfect, the deflection pattern of a beam of paramagnetic Li atoms of unit peak intensity, $I(s, H, v)$, should consist of two images of the undeflected displacement profile, $I(s)$, of 0.5 peak intensity displaced symmetrically right and left a distance $s(v)$ given by Eq. (4). The true $I(s, H, v_o)$ would be somewhat broadened due to the finite velocity spread transmitted by the SDVA. Even in this case, however, $I(s, H, v_o)$ should be symmetric about $s = 0$ and the peaks in $I(s, H, v_o)$ should scale as $v_o^{-2}$ to lowest order ignoring the dependence of field gradient on spatial position. The absence of either feature in the Li atom deflection patterns shown in panels (d) and (e) of Fig. 4 illustrate that calculation of $I(s, H, v_o)$ for the field gap configuration employed here would have to incorporate such second-order corrections as the very strong field inhomogenity and the probability that deflected species strike the poles.

Fortunately, however, the calculation of reactive scattering intensity,
$I_{\text{LiX}}(\theta, v)$, from experimental measurements is dependent only on the behavior of the deflection pattern within ±0.032 cm. of $s = 0$ [i.e., the tungsten ribbon width]. In these experiments, the intensity is recorded for an $s = 0$ detector placement as a function of LAB recoil speed and angle at zero magnetic field, $I_0(\theta, v)$, and at the "standard field", $I_H(\theta, v)$. The scattered LiX product intensity is then calculated as

$$I_{\text{LiX}}(\theta, v) = \left[ I_H(\theta, v) - T_{\text{Li}}(v) I_0(\theta, v) \right] / \left[ T_{\text{LiX}}(v) - T_{\text{Li}}(v) \right]$$

(5)

in terms of the transmissions of Li and LiX at the "standard field", e.g. $T_{\text{Li}}(v) = I_{\text{Li}}(s=0, H, v)$. For most reactions, of course, LiX is diamagnetic and $T_{\text{LiX}}(v) = 1$.

It is, of course, straightforward to measure the speed dependent transmission of the main Li beam at the "standard field". However, this is not quite the proper function for use in Eq. (5) because the Li atom transmission function is dependent on the displacement profile which, in turns, depends upon whether the detector is viewing the main Li beam or the scattered signal. Only in this latter case is the displacement profile determined by the geometries of slits L and F and the tungsten ribbon.

If the SDVA resolution were perfect and the higher order effects destroying the symmetry of the deflection patterns of Fig. 4 could be ignored, the form of $T_{\text{Li}}(v)$ could be readily understood. In this case, a plot of $T_{\text{Li}}(v)$ as a function of $s = s(v)$ [from Eq. (4)] would be superimposable upon a plot of the (undeflected) displacement profile. Figure 5 illustrates that this is indeed true for data collected on the Li beam and establishes that the apparatus constant of Eq. (4) is $K = 1.24 \times 10^5 \text{m-G}$. This good agreement presumably arises because the transmission function is finite only for small deflections [i.e., the displacement profile width] so that higher order corrections are unimportant. In view of the good agreement in Fig. 5,
the displacement profile of the scattered signal, shown in Fig. 6, was then employed in a similar way to calculate $T_{Li}(v)$ from Eq. (4) and the reactive scattering intensity from Eq. (5).

Li + NO$_2$

RESULTS AND DATA ANALYSIS

LiO Deflection Analysis

A molecular beam electric resonance study has established$^{22}$ that the ground state of LiO is $X^2\Pi$. A discussion in Ref. 5c indicates that this state would be expected to behave as a diamagnetic species under the crude deflection resolution employed here. In Hund's case (a), $^2\Pi_{3/2}$ would have no magnetic moment whereas $^2\Pi_{1/2}$ would exhibit a time-averaged magnetic moment dependent on the LiO product rotational quantum number, $g_J = 3/J(J+1)$. Since $J' \approx 20$ might be expected as typical$^{5c}$ with a random distribution in $M_J$, deflection of LiO($X^2\Pi$) should be negligible$^{23}$. Panels (b) and (c) of Fig. 7 show deflection patterns of species scattered from crossed beams of Li and NO$_2$ which confirm this expectation. Both panels show a deflected component, scattered Li atoms (cf. Fig. 4), and a second component whose deflection pattern coincides with the displacement profile of the undeflected beam. This "diamagnetic" Li-containing species in the scattered signal must correspond to product LiO($X^2\Pi$) because the NO$_2$ beam source conditions (Table III) corresponded to negligible (0.3% - calculated) N$_2$O$_4$ beam impurity.

Although the $X^2\Pi \rightarrow A^2\Sigma$ term energy, $T_e$, is quite large for HO, it is likely to be much smaller for LiO because the ground states of RbO and CsO are now known to be $X^2\Sigma$. Interestingly, this was first established
for CsO from magnetic and electric deflection analysis\textsuperscript{24} of scattering of Cs from NO\textsubscript{2}; it was later confirmed\textsuperscript{25} by ESR of matrix isolated CsO and RbO. The A\textsuperscript{2}Σ state of LiO has never been observed experimentally, although a recent CI calculation\textsuperscript{26a} gave \( T_e = 27.9 \text{kJ/mole}. \) Panel (a) of Fig. 7 shows the deflection pattern of species scattered from Li + NO\textsubscript{2} at a relatively low LAB recoil speed. In addition to the undeflected LiO(X\textsuperscript{2}Π) component, this shows a clearly resolved deflected component which cannot correspond to Li atoms because these are deflected beyond the scale of the figure at this slow speed. Although this data was very noisy and was not reproduced because of the inordinate difficulty of these deflection pattern measurements and because its significance was not appreciated until the subsequent data analysis steps, the position of the deflected peak corresponds to \( g_J = 1.5 \pm 0.5 \) if it is analyzed assuming the mass of LiO. Any deflection of LiO(X\textsuperscript{2}Π) due to \( 2\text{Π}_{3/2} \) in Hund's case (a), due to an \( \Lambda \)-S uncoupling in going to Hund's case (b), or due to a perturbation in higher vibrational levels by A\textsuperscript{2}Σ would likely be broadened due to a wide distribution in \( g_J \). The contrasting sharpness of the deflected pattern in panel (a) indicates that it must be due to formation of LiO(A\textsuperscript{2}Σ) from Li + NO\textsubscript{2} which lives long enough to traverse the deflecting field because: (1) no other state of LiO is likely to be low enough in energy to be populated by reaction; and (2) \( g_J = 2 \) for LiO(A\textsuperscript{2}Σ) in this high field limit in the absence of perturbation by LiO(X\textsuperscript{2}Π).

This establishes two properties of LiO(A\textsuperscript{2}Σ). By energy conservation, its term energy is related to \( \Delta D_o \), the exoergicity of the ground state reaction channel, by

\[
T_e + W' + E' = W + E + \Delta D_o
\]

where \( E \) refers to translational energy, \( W \) to rotational and/or vibrational excitation, unprimed quantities to reactants, and primed quantities to products. This establishes that \( T_e \leq 64 \text{kJ/mole} \) using the average value of \( E \); a more cautious analysis indicates \( T_e \leq \sim 90 \text{kJ/mole} \) recognizing
the uncertainty in $\Delta D_0$ and distribution in E. Additionally, the radiative lifetime of LiO($A^2\Sigma$) must be $\geq 3.5 \times 10^{-4}$ sec, the flight time through the deflecting field, in agreement with the small calculated oscillator strengths reported in Ref. 26 b ($\tau \sim 0.25$ sec). This, of course, also establishes $X^2\Pi$ and $A^2\Sigma$ as products of Li + NO$_2$, but says nothing regarding the relative product channel yields. The actual $^2\Pi$ component in panel (a) of Fig. 7 was only about 10% of that in panel (c) for $\Theta = 30^\circ$. Ref. 5(c) reported that the paramagnetic Li species component was comparable to but somewhat less than the diamagnetic component for large angles of scattering of Li from NO$_2$ ($\Theta > 50^\circ$). Data reported in Ref. 10 indicates that this paramagnetic component peaks at low LAB recoil speeds, i.e. that it includes major contributions from inelastic scattering of Li atoms or production of LiO($A^2\Sigma$) product.

**Product Recoil Distribution**

**Data Analysis Procedure**

Results of the LiO deflection analysis failed to indicate any measurable deflection of LiO($X^2\Pi$). Another product, LiO($A^2\Sigma$), is formed at low LAB recoil velocities where its transmission through the field is zero. Energy conservation should effectively preclude the formation of this excited state at higher LAB recoil velocities where its transmission would be finite; this is corroborated by panels (b) and (c) of Fig. 7 which fail to show any evidence of this state in the deflection patterns. In view of this, reactive scattering data which were collected were analyzed by means of Eq. (5) with $T_{LiX}(v) = 1$ to obtain the LiO recoil flux probability density produced by the reaction:

$$^7\text{Li} + \text{NO}_2 \rightarrow ^7\text{LiO}(X^2\Pi) + \text{NO}. \quad (1)$$
Figures 8 and 9 show the data which were obtained in this way. As remarked previously, each data point has been multiplied by $\beta(\Theta)$ to correct for the viewing factor and has been divided by the speed to correct for the SDVA transmission. The data were collected by first scanning angle, at one fixed SDVA speed, in order to normalize the data which were subsequently collected by varying the SDVA speed at each angle. Periodic measurements were taken at standard positions in both the angular and speed scans in order to correct for possible drifts in beam intensities or detector sensitivity with time.

The LAB "differential cross section" for LiO product scattering into solid angle $\Omega$ to $\Omega + d\Omega$ with recoil speed of $v$ to $v + dv$, 

$$\left(\frac{3\sigma}{2\Omega \delta v}\right),$$

which is measured is related to the corresponding CM differential cross section, $\frac{\partial^3\sigma}{\partial^2w \partial w}$, by

$$\left(\frac{3\sigma}{2\Omega \delta v}\right) = \int_0^\infty \int_0^\infty \left(\frac{3\sigma}{2\delta w \delta w}\right) \frac{v^2}{w^2} P(v_1, v_2) dv_1 dv_2. \quad (7)$$

Here, $v_1$ and $v_2$ are the speeds of particles in beams 1 and 2,

$$P(v_1, v_2) = gF(E) \rho_1(v_1) \rho_2(v_2) \quad (8)$$

is the probability that a particular CM $\rightarrow$ LAB velocity vector transformation diagram contributes to the scattering, $g = |\vec{v}_1 - \vec{v}_2|$ is the relative collision speed, $E = \mu g^2/2$ is the relative collision energy in terms of the reactant reduced mass, $\mu$, and $F(E)$ is the energy dependence of the total reactive cross section. In the absence of velocity selection of the Li beam or, at least, measurements at different beam temperatures, the data are insensitive to any dependence of the $(\theta, w)$ distributions on $E$ so that Eq. (7)
is employed assuming $\frac{\partial^3 \sigma}{\partial \omega \partial \omega}$ is independent of $E$. Results on $K + I_2$ and $CH_3I$ obtained with a velocity selected $K$ beam suggest that this is typically a good approximation for the limited range of $E$ which contributes to the scattering.

In their recent review of crossed beams chemical dynamics studies, Farrar and Lee classified experiments of the type listed in Table I as "E" if at least one incident beam were velocity selected (e.g., Refs. 27-31), as "F" otherwise (e.g., Refs. 32-34). Since the present series of measurements are of class "F", it is instructive to examine the disadvantages of class "F" relative to class "E" in order to better define the information content of the data. One disadvantage is the broader distribution in collision energies in class "F"; Fig. 10 shows the distribution in $E$ for $Li + NO_2$ calculated for $F(E) = 1$ using the beam properties listed in Table III. This indicates 25%, 50%, and 75% probabilities that $E$ is less than or equal to 12, 20, and 30 kJ/mole so that a reasonable indication of the collision energy is $20 \pm 9$ kJ/mole. In the absence of measurements at different beam temperatures, the form of $F(E)$ is only weakly constrained by the data, and this introduces some uncertainty into the inferred form of $\frac{\partial^3 \sigma}{\partial \omega \partial \omega}$. The second disadvantage of class "F" is the broader distribution in $CM \rightarrow LAB$ velocity vector transformation diagrams which further degrades the resolution of the $CM$ recoil distribution. This is not too serious a problem, however, when a beam of light, fast particles is crossed by a beam of heavy, slow particles because the distribution in center-of-mass velocities (centroids), which defines the origin of the $CM$ coordinate system, spans only a small portion of $LAB$ recoil velocity space. This is illustrated for $Li + NO_2$ in Fig. 11.
The data analysis objective, of course, is to infer the form of the CM differential cross section from the measurements via Eq. (7). This has been approached in a couple of ways in the literature. Siska describes an iterative unfolding technique; however, experience in our laboratory with this technique in another application indicates poor convergence unless the data is smoothed. Alternatively, \( \frac{\partial^3 \sigma}{\partial \Omega \partial \omega} \) can be expanded in a series of independent functions. Bernstein and co-workers (e.g., Ref. 35) used Legendre polynomials in angle and recoil speed, whereas Herschbach and co-workers (e.g., Refs. 7 and 33) used Legendre polynomials in angle and fourth order Laguerre polynomials in recoil speed. We have adopted the latter approach and expanded the CM differential cross section as

\[
\frac{\partial^3 \sigma}{\partial \Omega \partial \omega} = 4 \sum_{i=0}^{n_L-1} \sum_{j=0}^{n_P-1} a_{ij} P_i(\cos \theta) L_j^{(4)}(2\omega / \omega_0)(\omega^2 / \omega_0^2) e^{-\omega / \omega_0} \tag{9}
\]

where \( \theta = 0^\circ \) is defined by the incident Li atom direction in the CM coordinate system. These polynomials are normalized such that \( P_i(1) = 1 \) and \( L_j^{(4)}(x) \) has a coefficient of \((-1)^j/j! \) for the \( x^j \) term. The procedure is to evaluate \( \left< \frac{\partial^3 \sigma}{\partial \Omega \partial \omega} \right> \), subject to the energy conservation expressed in Eq. (6), by numerical integration of Eq. (7) by the Zaremba method of Ref. 25 and to determine the \( a_{ij} \) coefficients by minimizing

\[
\chi^2 = \sum_{i=1}^{N_D} \left[ I_i \chi(\theta_i, \nu_i) - \left< \frac{\partial^3 \sigma}{\partial \Omega \partial \omega} \right> \right]^2 / \delta_i^2 \tag{10}
\]

The sum is over all \( N_D \) data points, \( \delta_i \) is the standard deviation of the \( i \)-th data point, and \( \nu = N_D - n_P n_L \) is the degrees of freedom in the fit.

This Laguerre polynomial expansion has advantages and disadvantages relative to a Legendre expansion in \( \omega \) because of the \( \omega_0 \) parameter in the
weighing factor. The disadvantage is that optimization of $w_o$ requires a non-linear least-squares minimization procedure whereas the $a_{ij}$'s can be obtained by a linear procedure for fixed $w_o$. The advantage is that one can obtain quite similar fits to the data and inferred forms of $\frac{\partial^3 \sigma}{\partial^2 \omega \partial \omega} w$ for quite different sets of $a_{ij}$'s corresponding to differing $w_o$ values. This provides confidence that the inferred CM differential cross section is not dependent on the particular expansion functions chosen.

The expansion function given in Eq. (9) makes no assumption about separability of the CM recoil distributions into angle and energy; fits to this function are described as COUPLED. Since this is an interesting feature of the reaction, the data analysis also examined fits to an UNCOUPLED expansion

$$\frac{\partial^3 \sigma}{\partial^2 \omega \partial \omega} = \sum_{i=0}^{n_\ell-1} b_i P_i(\cos \theta) \left\{ \sum_{j=0}^{n_\ell-1} c_j (w^2 / w_o^2)e^{-w / w_o} L_j^{(4)}(2w / w_o) \right\}.$$  \hspace{1cm} (11)

Another interesting feature is the presence or absence of symmetry about $\theta = 90^\circ$. This could be checked by imposing this symmetry on Eqs. (9) or (11) via an expansion in even Legendre polynomials only; these fits are labeled COMPLEX. Finally, various forms of $F(E)$ were tried in an attempt to assess the uncertainty introduced by the breadth of $P(E)$; these are described as:

$$F(E) = E^{-1/3} \quad \text{(ORBITING)},$$

$$F(E) = 1 \quad \text{(FLAT)},$$

$$F(E) = h(E-E*) \quad \text{(STEP-E*)},$$

and

$$F(E) = (1-E*/E)h(E-E*)(\text{LINE-OF-CENTER-E*}).$$ \hspace{1cm} (12)
For a fixed $w_0$, the procedure is to start with a limited number of polynomials and to alternately increase $n_P$ or $n_L$ by one. This is continued so long as the F-test\textsuperscript{37} indicates a significant improvement in $\chi^2$, i.e. a 90% confidence level that the improvement in $\chi^2$ isn't due to fitting random noise in the data. CM product recoil distributions evaluated in this way are reported in Ref. 10. Although the fits to the data were good, the form of \[ \langle \frac{\partial^3 \sigma}{\partial^2 \Omega \partial v} \rangle \] was unconstrained outside of the limited angular and speed ranges spanned by the data of Figs. 8 and 9. This typically resulted in a $\partial^3 \sigma/\partial^2 \omega \partial w$ function which was inconsistent with the product angular distribution reported in Ref. 5. The angular distribution is easily calculated from Eq. (7) as

\[
\langle \frac{\partial^2 \sigma}{\partial^2 \Omega} \rangle = \int_0^\infty \langle \frac{\partial^3 \sigma}{\partial^2 \Omega \partial v} \rangle \, dv.
\] (13)
By itself, Eq. (13) is very ill-conditioned to determine the form of $\frac{\partial^3 \sigma}{\partial \omega^2} \omega \partial \omega$ solely from angular distribution measurements. However, it does provide significant constraints on the form of $\frac{\partial^3 \sigma}{\partial \omega^2} \omega \partial \omega$ obtained by fitting product velocity analysis data. Thus, the data analysis procedure employed simultaneously fit LiO product velocity analysis measurements via Eq. (7) and angular distribution measurements via Eq. (13) to CM product distributions given by Eqs. (9), (11), and (12) by minimizing $\chi^2$ of Eq. (10) where the sum was over both types of data points.

Data Analysis Results

The Li + NO$_2$ beam conditions are listed in Table III. As the first paper of a series, a variety of CM functions, listed in Table IV, were fit to the data in order to better define the information content of the measurements. The uncertainty, $\delta_i$, of any LiO recoil velocity data point shown in Figs. 8 and 9 was difficult to assess. In order to simultaneously fit this data and the LiO product angular distribution data of Ref. 5c, which are shown in Fig. 12 with their measured standard deviations, each data point in Figs. 8 and 9 was assigned a $\delta_i = 0.6$. This arbitrary assignment of $\delta_i$ determined the magnitude of $\chi^2$. 
The measurements shown in Figs. 8 and 9 are marginally sensitive to the form of \( F(E) \) because LAB velocities corresponding to both positive and negative values of \( \theta \) must be fit to a \( \frac{d^3\sigma}{d\theta^2 \omega \, d\omega} \) with cylindrical symmetry about \( \theta = 0^\circ \). Table IV indicates that \( \chi^2 \) decreases in the sequence: COUPLED-ORBITING, COUPLED-FLAT, COUPLED-LINE-OF-CENTER-5. Although this suggests some predilection for a small activation energy, the form of \( \frac{d^3\sigma}{d\theta^2 \omega \, d\omega} \) which is presented as the "best" fit is the COUPLED-FLAT which makes the weakest assumption about the behavior of \( F(E) \). The parameters for this fit are listed in Table V. Fits to the \( \text{LiO} \) product velocity measurements are shown in Fig. 8 and 9 and to the \( \text{LiO} \) angular distribution in Fig. 12. A polar plot of the inferred \( \frac{d^3\sigma}{d\theta^2 \omega \, d\omega} \) is shown in Fig. 13. All of the COUPLED fits listed in Table IV with \( \chi^2 < 1.3 \) gave plots quite similar to Fig. 13.

The data point locations shown in Fig. 13 indicate that the data of Figs. 8 and 9 determine the form of \( \frac{d^3\sigma}{d\theta^2 \omega \, d\omega} \) for \( \theta \leq 90^\circ \). The behavior for \( \theta > 90^\circ \), however, is largely an analytical continuation into the backward hemisphere. There is no data to support the secondary peak at \( \theta = 180^\circ \) nor the long tail in \( \omega \) between 90° and 120°.

Nevertheless, the data clearly establish the absence of symmetry about \( \theta = 90^\circ \); this is indicated by the \( \chi^2 \) entries for the COMPLEX functions listed in Table IV. Figure 12 indicates that it is impossible to fit the \( \text{LiO} \) product angular distribution with such a symmetric CM function. Figure 13 also shows a weak \( \theta - \omega \) coupling in the recoil distribution with higher \( \text{LiO} \) recoil speed favored at smaller scattering angle. Table IV indicated that this was corroborated by the significantly poorer \( \chi^2 \) obtained with UNCOUPLED functions which failed to provide as good a fit to the data of Fig. 9 at intermediate angles [\( \theta = 40^\circ - 70^\circ \)].
The CM differential cross section shown in Fig. 14 indicates a sharp forward scattering of the LiO product. The behavior of this function for \( \theta \leq 90^\circ \) is reliably determined by the data of Figs. 8 and 9. The average behavior for \( \theta > 90^\circ \) is also determined by fitting the LAB angular distribution of Fig. 12, although the structure in this region might be an artifact of the fitting procedure.

The distribution in translational recoil energy of the products is easily calculated as

\[
P(E') = 2\pi \int_0^{\theta^*} \frac{\partial^3 \sigma}{\partial \theta \partial \omega \partial E} \sin \theta \ d\theta
\]  

with

\[
\frac{\partial^3 \sigma}{\partial \omega \partial E'} = \frac{\partial^3 \sigma}{\partial \omega \partial w} \left| \frac{dw}{dE'} \right|
\]

Panel (a) of Fig. 15 shows \( \partial^3 \sigma / \partial \omega \partial E' \) for \( \theta = 0^\circ, 45^\circ, \) and \( 90^\circ \) in order to illustrate the degree of recoil angle and energy coupling in the CM contour map shown in Fig. 13. Ideally, the integration in Eq. (14) should extend to \( \theta^* = 180^\circ \). However, the data of Figs. 8 and 9 only determine the exact form of \( \partial^3 \sigma / \partial \omega \partial E' \) out to about \( 90^\circ \), and this is the largest source of uncertainty in the inferred form of \( P(E') \). The extent of this uncertainty for Li + NO\(_2\) is shown in panel (b) of Fig. 15 where \( P(E') \) functions calculated by integrating Fig. 13 to \( \theta^* = 90^\circ \) and \( 180^\circ \) are compared. This panel also illustrates that the uncertain form of \( F(E) \) [e.g., fits A and B] represents less uncertainty in \( P(E') \). Panel (c) shows the integrated form of the preferred \( P(E') \) function [the solid curve of panel (b)], i.e. the probability that \( E' \) is less than or equal to a certain amount. This "best" inferred \( P(E') \) corresponds to LiO + NO most probable, median, and mean recoil energies of 16, 29, and 33 kJ/mole, respectively.
DISCUSSION

In summary, LiO($X^2\tilde{I}$) and LiO($A^2\Sigma$) are established as product channels of the Li + NO$_2$ bimolecular reaction. With respect to the ground state channel [Reaction (I)], the results indicate a direct reaction mechanism with a forward-peaked product angular distribution [LiO recoil preferentially along the original Li velocity]. There is a weak coupling of the recoil angle and energy distributions with higher $E'$ favored at smaller $\theta$. If the reaction energy were partitioned statistically, $P(E')$ should vary as $(E' - E)^n$ at high $E'$, where $n = 3 - 5$ depending on the structure of the activated complex and $E' \approx \Delta D_0 + \langle E \rangle + \langle W \rangle$. Although one may expect some deviations from this prediction due to failure of the classical level densities and possible subsequent product interactions in the decay of a tight complex, the large discrepancy between this statistical prediction and the measured $P(E')$ which is shown in panel (c) of Fig. 15 confirms the direct character of the reaction mechanism. This measured $P(E')$ corresponds to a relatively high conversion of reaction energy into product recoil, with $\langle E' \rangle / [\Delta D_0 + \langle E \rangle + \langle W \rangle] = 0.45$.

Figure 16 summarizes the thermochemistry of Reaction (I) and includes rough estimates of the energies of the ground singlet and lowest excited triplet states of lithium nitrite. These were estimated from an ionic bonding model described in Ref. 24, using the correct NO$_2$ electron affinity, which might overestimate the Li-NO$_2$ bond energy. Nevertheless, $D_0$(Li-NO$_2$) is clearly substantial ($\sim 400$ kJ/mole) so that the ground electronic state of LiNO$_2$ represents a deep chemical well in the potential surface for Reaction (I). Furthermore, this state of LiNO$_2$ correlates with the Li + NO$_2$ reactants for any approach geometry because it is formed by transfer of the 2s Li valence electron into the $6a_1$ molecular orbital of NO$_2$. Thus, the direct mechanism
of the Li+NO₂ reaction appears anomalous. The accessible, deep well in the ground state potential surface as well as the relatively small reaction exoergicity would ordinarily dictate a collision complex mechanism. This is the behavior which has been observed in a number of analogous alkali reactions including: alkali + alkali halide\(^{39,40}\); alkali + SO₂, CO₂, O₂[non-reactive scattering only]\(^{41}\); alkali + SnCl₄, SF₆\(^{33}\); alkali + Group IIB halides\(^{34}\); and alkali halide + alkali halide\(^{42}\). The reason for the contrasting direct Li+NO₂ reaction mechanism remains uncertain. It might reflect a truly surprising reaction mechanism on the ground state potential surface. On the other hand, Li and NO₂ approach on a spin triplet potential surface in 75% of the trajectories. If reaction probabilities were comparable for the two surfaces, reactions on the triplet surface would dominate the observations. Figure 16 indicates that direct reaction through a Li\(^+\left(1S\right)\)-NO₂\(^-\left(3B₁\right)\) intermediate is plausible. The fact that NO₂\(^-\left(3B₁\right)\) is formed by transfer of the Li valence electron into the antibonding 2b₁ \(\pi\) orbital on NO₂ is also consistent with the relatively high product recoil energies which are measured. Reaction through the triplet spin configuration was regarded as unlikely in Ref. 5c because of the relatively small total cross section for Reaction (I). This objection is considerably weakened, however, by the present observation that much of the wide-angle scattering of paramagnetic Li-species is due to LiO(A\(^2Σ\)) and/or inelastically scattered Li. The strong quenching of the glory undulations in the Li + NO₂ total collision cross section which is reported in Ref. 44 would also be consistent with reaction on the triplet as well as the singlet potential surface.
Special dynamical features of some H atom reactions have been discussed in terms of an approximate separability of the motion of the light H atom from that of the heavier atoms. Although the speed ratios would be smaller, the relatively light Li mass suggests that comparison of H and Li reaction dynamics might be informative in certain cases. Similarities of this sort are discussed for H and Li + alkali fluorides in Ref. 40, for which the potential surfaces might be qualitatively similar. In contrast, the H and Li + NO₂ potential surfaces should have much less in common in view of: (a) the likely ionic intermediate in the Li reaction; (b) the quite different ratios of reaction exothermicity to collision complex stability; and (c) complications due to triplet as well as singlet potential surfaces in either reaction. Nevertheless, the Li+NO₂ product recoil distributions reported here are similar to those reported for H and D + NO₂ in Ref. 45. An isotope effect is seen in the product angular distribution, with the heavier D producing sharper forward scattering; Fig. 14 shows that the results reported here for Li + NO₂ follow this trend. Moreover, panel (c) of Fig. 15 illustrates the close similarities in the high E' portions of P(E') for H, D, and Li + NO₂.

ACKNOWLEDGMENTS

We are indebted to Ms. Joni Gray and Dr. Richard Behrens, Jr. for assistance with the data analysis program. All data were collected while this program was supported through the Lawrence Berkeley Laboratory, who have also covered publication cost. Data analysis and interpretation was completed at the Ames Laboratory and supported by the USERDA under contract No. W-7405-eng-82.
REFERENCES


5. (a) D. D. Parrish and R. R. Herm, J. Chem. Phys. 49, 5544 (1968); (b) 51, 5467 (1969); (c) 54; 2518 (1971).


11. Purchased from Brunswick Corporation, Technical Products Division, Skokie, Ill.

12. Although it may have been peculiar to the particular background gas in our apparatus, detection sensitivity was poor unless this filament was properly "activated". This consisted in heating it overnight at 1630°K followed by a brief exposure to ~ 2.5 x 10^{-6} torr of O2 at 2375°K immediately prior to an experiment.

21. The distinction between ν and ν₀ was only important in discussing the SDVA calibration. No attempt is made to deconvolute the SDVA bandpass from reactive scattering measurements.
23. Remarks in Ref. 5c to the effect that \(^{2}\Pi_{3/2}\) deflection might be partially resolvable do not apply here because of the poorer deflection resolution in the present study.


36. We are indebted to Dr. K. T. Gillen for assistance on this aspect of the data analysis program.


38. We are indebted to Dr. R. Behrens, Jr. for modifying the data analysis program to simultaneously fit product velocity analysis and angular distribution measurements.


46. It seemed inappropriate to compare \( P(E') \) at low \( E' \) because of the finite activation energy for the reverse reaction in H, D+NO\(_2\).
Table I. LAB product velocity measurements and derived CM recoil distributions reported for alkali atom reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>K + HBr, DBr</td>
<td>30</td>
</tr>
<tr>
<td>K + Br₂</td>
<td>29, 32</td>
</tr>
<tr>
<td>K + I₂</td>
<td>27</td>
</tr>
<tr>
<td>K + CH₃I</td>
<td>28</td>
</tr>
<tr>
<td>K + CF₃I</td>
<td>31</td>
</tr>
<tr>
<td>K, Rb, Cs + SF₆, SnCl₄</td>
<td>33</td>
</tr>
<tr>
<td>K + ZnCl₂, ZnI₂, CdI₂, HgBr₂, HgI₂</td>
<td>34</td>
</tr>
</tbody>
</table>
Table II. Apparatus dimensions (cm).

<table>
<thead>
<tr>
<th>Item</th>
<th>Fig. 1</th>
<th>Width</th>
<th>Height</th>
<th>Distance from BIR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Li oven</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Source slit</td>
<td>U</td>
<td>0.031</td>
<td>0.22</td>
<td>3.5</td>
</tr>
<tr>
<td>Collimation slit</td>
<td>T</td>
<td>0.15</td>
<td>0.45</td>
<td>1.7</td>
</tr>
<tr>
<td><strong>Gas oven</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Source slit</td>
<td>N</td>
<td>0.12</td>
<td>0.64</td>
<td>3.2</td>
</tr>
<tr>
<td>Collimation slit</td>
<td>M</td>
<td>0.34</td>
<td>0.60</td>
<td>1.3</td>
</tr>
<tr>
<td><strong>Velocity analyzer slit</strong></td>
<td>L</td>
<td>0.093</td>
<td>0.46</td>
<td>3.8</td>
</tr>
<tr>
<td><strong>Deflecting magnet slit</strong></td>
<td>F</td>
<td>0.065</td>
<td>0.24</td>
<td>14.1</td>
</tr>
<tr>
<td><strong>Surface Ionization Filament</strong></td>
<td>A</td>
<td>0.064</td>
<td>2.5</td>
<td>38.9</td>
</tr>
</tbody>
</table>

* Full angular widths at 90%, 50%, and 10% peak intensities were: 2.0°, 3.0°, 4.6° (Li beam); 5.3°, 11°, 24° (gas beam).
Table III. Beam conditions \( a \) for \( \text{Li} + \text{NO}_2 \rightarrow \text{LiO}(X^2\Pi) + \text{NO} \).

<table>
<thead>
<tr>
<th>Lithium Beam:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>1150(^\circ)K</td>
</tr>
<tr>
<td>Pressure ( b )</td>
<td>0.9 torr</td>
</tr>
<tr>
<td>( % \text{Li}_2 ) ( b )</td>
<td>0.8</td>
</tr>
<tr>
<td>( u )</td>
<td>390 m/sec</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>1730 m/sec</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NO(_2) Beam:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>350(^\circ)K</td>
</tr>
<tr>
<td>Pressure</td>
<td>9.5 torr</td>
</tr>
<tr>
<td>( % \text{N}_2\text{O}_4 ) ( b )</td>
<td>0.3</td>
</tr>
<tr>
<td>( u )</td>
<td>120 m/sec</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>360 m/sec</td>
</tr>
<tr>
<td>Average internal energy</td>
<td>4.9 kJ/mole</td>
</tr>
</tbody>
</table>

Relative Collision Energy:
- Most probable | 14 kJ/mole |
- Median | 20 kJ/mole |
- Mean | 24 kJ/mole |

Reaction Exoergicity:
\[ \Delta D_0 \quad 44\text{kJ/mole} \quad c \]

\( a \) \( u \) and \( \alpha \) are beam parameters of Eq. (2).
% dimer refers to calculated equilibrium concentrations in the source.


D. L. Hildebrand, J. Chem. Phys. 57, 4556 (1972) quotes $D_0(LiO) = 337\pm 6$ kJ/mole corresponding to $\Delta D_0 = 38\pm 6$ kJ/mole. The higher end of this range, 44 kJ/mole, was used in data analysis in order to minimize the number of energy conservation rejections [Eq. (7)]. The JANIF value of $\Delta D_0 = 21\pm 21$ kJ/mole appears to be too low.
Table IV. Summary of Li + NO₂ data analysis.

<table>
<thead>
<tr>
<th>CM Function</th>
<th>Label</th>
<th>w₀</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>COUPLED-FLAT</td>
<td>660</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1160</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A 700</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>COUPLED-ORBITING</td>
<td>560</td>
<td>1.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1260</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>1.23</td>
<td></td>
</tr>
<tr>
<td>COUPLED-LINE-OF-CENTER-5</td>
<td>580</td>
<td>1.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>780</td>
<td>1.21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B 680</td>
<td>1.17</td>
<td></td>
</tr>
<tr>
<td>COUPLED-LINE-OF-CENTER-10</td>
<td>700</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>COUPLED-LINE-OF-CENTER-20</td>
<td>700</td>
<td>1.43</td>
<td></td>
</tr>
<tr>
<td>COUPLED-LINE-OF-CENTER-30</td>
<td>700</td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td>COUPLED-FLAT-COMPLEX</td>
<td>760</td>
<td>1.82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1160</td>
<td>1.82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C 860</td>
<td>1.82</td>
<td></td>
</tr>
<tr>
<td>COUPLED-ORBITING-COMPLEX</td>
<td>1160</td>
<td>1.96</td>
<td></td>
</tr>
<tr>
<td>UNCOUPLED-FLAT</td>
<td>440</td>
<td>1.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td>640</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>D 530</td>
<td>1.41</td>
<td></td>
</tr>
<tr>
<td>UNCOUPLED-ORBITING</td>
<td>1160</td>
<td>1.79</td>
<td></td>
</tr>
</tbody>
</table>

\( w₀ \) is the parameter of Eqs. (9) and (11) in m/sec. Three entries for one CM function indicates that a search over the range of the first two converged on the third.
<table>
<thead>
<tr>
<th></th>
<th>$L_0^{(4)}$</th>
<th>$L_1^{(4)}$</th>
<th>$L_2^{(4)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_0$</td>
<td>0.092</td>
<td>2.006</td>
<td>-0.617</td>
</tr>
<tr>
<td>$P_1$</td>
<td>2.508</td>
<td>-0.589</td>
<td>-0.011</td>
</tr>
<tr>
<td>$P_2$</td>
<td>-2.454</td>
<td>2.625</td>
<td>-0.837</td>
</tr>
<tr>
<td>$P_3$</td>
<td>5.827</td>
<td>-3.843</td>
<td>1.001</td>
</tr>
<tr>
<td>$P_4$</td>
<td>-0.799</td>
<td>1.133</td>
<td>-0.398</td>
</tr>
</tbody>
</table>

The $a_{ij}$ coefficients of Eq. (9), in arbitrary units, for $w_o = 700$ m/sec.
FIGURE CAPTIONS

Fig. 1. Schematic diagram of the apparatus viewed from above the plane defined by the two beams. Items not identified in the text arc:
D- copper box for electrical shielding of the surface ionization mass spectrometer unit; P-stainless steel shields; S-solenoid activated beam flag; W-copper cold shield.

Fig. 2. Fits (solid curves) to measured Li beam speed distributions (data points - corrected for SDVA transmission) obtained by convoluting Maxwell-Boltzman flux density speed distribution over bandpass function of the SDVA. Velocity scale is reduced to be 1.0 at peak of distribution. This is some of the data which was used in calibrating the analyzer. Panels correspond to data collected with Li beam source pressures (determined by lower chamber temperature) and temperatures of: (a) 4.7 x 10^{-4} torr, 1031°K; (b) 2.4 x 10^{-3} torr, 1040°K; (c) 6.4 x 10^{-3} torr, 1048°K.

Fig. 3. Data points show measured Br₂ beam speed distributions obtained for source temperature of 373°K and two source pressures. Solid curves show fits obtained to Eq. (2) with α = 200 m/sec by convoluting over selector bandpass recognizing that data refers to a number density detector. Dashed curve shows corresponding thermal distribution function.

Fig. 4. Drawing (dimensions in cm) of inhomogeneous deflecting electromagnet (a) as well as displacement profiles (b) and deflection patterns (c-e) of scattered signals from crossed beams of Li and Br₂ at various LAB angles and speeds. Panels (c-e) were all recorded at the "standard field" strength produced by a 3000
amp-turn magnetomotive force and are normalized to a unit peak intensity displacement profile.

**Fig. 5.** Circles (error bars flagged to left) show the measured displacement profile of the Li beam. Squares (error bars flagged to right) show the measured Li atom transmission versus v for the "standard field" plotted versus s=s (v) [ Eq. (4)] which provided the best fit to the circles (see discussion in text). Solid curve has no theoretical significance.

**Fig. 6.** Circles show measured displacement profile of the scattered signal. Solid curve shows theoretical prediction calculated from widths and positions of slits L and F and the tungsten ribbon detector. In conjunction with the magnet calibration established in Fig. 5, this solid curve was used to calculate the Li atom transmission function for the scattered signal.

**Fig. 7.** Data points show deflection patterns [for the "standard field"] of the scattering from Li + NO₂: (a) θ = 30°; (b) θ = 30°; (c) θ = 30°(circles) and 60° (squares). Panel (c) has been re-normalized to unit peak height; actual transmissions were 50% (30°) and 70% (60°). Solid curves show the displacement profile of Fig. 6 normalized to the undeflected components.

**Fig. 8.** Data points show the LAB LiO product flux probability density speed distribution from Li + NO₂ for LAB scattering angles from -15.6° to 24.4°; open and closed data symbols alternate at successive angles. Solid and dashed curves show fits to the data obtained with COUPLED-FLAT (Fit A) and UNCOUPLED-FLAT (Fit D) CM differential cross sections, respectively.

**Fig. 9.** LAB data for θ from 29.4° to 99.4°; conventions as in Fig. 8.
Fig. 10. Solid curves show the distribution in collision energy, $P(E)$ (ordinate on left), as well as $\int_0^E P(x)dx$ (ordinate on right). Solid points indicate collision energies sampled during numerical integration for data analysis via Eq. (7); the ordinate of each point gives (in arbitrary units only) the probability of that particular CM $\to$ LAB velocity vector transformation diagram evaluated from Eq. (8). All calculations were performed for the Li $+$ NO$_2$ beam parameters given in Table III with $F(E) = 1$.

Fig. 11. Contours show lines of constant LiO flux intensity in the LAB coordinate system evaluated as $\frac{\partial^3 \sigma}{\partial \Omega \partial v}$ from Eq. (7) for the COUPLED-FLAT CM function (Fit A of Table IV). Black triangle denotes an intensity of 100; successive contour lines denote intensities of 90, 80, 70, 60, 50, 40, 30, 20, 10, and 5. Vectors show $\vec{v}_1$, $\vec{v}_2$, and $\vec{g}$ which maximize Eq. (8): $v_1 = v_{Li} = 2730$ m/sec; $v_2 = v_{NO_2} = 483$ m/sec. Fifty percent of the Li $+$ NO$_2$ centroid vectors terminate within the cross-hatched area.

Fig. 12. Data points show LiO product angular distribution reported in Ref. 5c. Solid and dashed curves show COUPLED-FLAT (Fit A) and COUPLED-FLAT-COMPLEX (Fit C), respectively.

Fig. 13. Solid lines show contours of constant $\frac{\partial^3 \sigma}{\partial \Omega \partial w}$ LiO CM differential cross section provided by the COUPLED-FLAT Fit A. Black triangle denotes a magnitude of 100; successive contour lines denote magnitudes of 90, 80, 70, 60, 50, 40, 30, 20, 10, and 5, with 50 and 5 shown as extra heavy. Dashed line traces the most probable w as a function of $\theta$. Data points locate ($\theta$, w) points obtained from the $(\theta$, v) of each data point of Figs. 8 and 9 for the most probable CM $\to$ LAB transformation diagram (Fig. 11).
with the following convention: O, +, or X if the LiO CM differential cross section obtained from a nominal LAB → CM inversion falls within, above, or below, respectively, the adjacent contours.

Fig. 14. Solid curve shows the LiO CM differential cross section, obtained by integrating \( \frac{d^3 \sigma}{d\omega dE} \) of Fig. 13 over \( \omega \), normalized to unity at \( \theta = 0^\circ \). Dashed and dotted curves show the corresponding results for D + NO₂ and H + NO₂, respectively, reported in Ref. 45; all three curves have been normalized to agree at \( \theta = 30^\circ \).

Fig. 15. Product recoil energy probability density distributions for Li + NO₂ → LiO(X²Π) + NO, all normalized to unit area under the curves. (a) \( \frac{d^3 \sigma}{d\omega dE} \) [Eq. (15)] evaluated from Fig. 13 at \( \theta = 0^\circ \) (solid curve), 45° (dashed curve), and 90° (dotted curve).

(b) \( P(E') \) from Eq. (14) for: COUPLED-FLAT [Fit A], \( \theta^* = 90^\circ \) (solid curve); COUPLED-FLAT [Fit A], \( \theta^* = 180^\circ \) (dotted curve); COUPLED-LINE-OF-CENTER-5 [Fit B], \( \theta^* = 90^\circ \) (dashed curve).

(c) Solid curve of panel (b) is presented again, as well as \( \int_0^{E'} P(x) dx \) (ordinate on right). Dashed curve, normalized to same peak height, is the high \( E' \) portion of \( P(E') \) reported for H, D + NO₂ in Ref. 45. Dotted curve shows \( (81 - E')^3 \) normalized to Li + NO₂ \( P(E') \) at \( E' = 50 \) kJ/mole.

Fig. 16. Thermochemistry of Li+NO₂ → LiO(X²Π) + NO reaction from Table III. Also shown are the energies of the ground singlet and lowest excited triplet states of lithium nitrite estimated from ionic bonding model in Ref. 24.
LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.