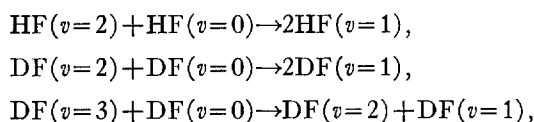
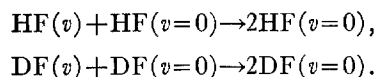


of the following reactions:

resonance:



complex formation:



CONCLUSIONS

The evidence indicates that at the onset of laser emission, collisional deactivation is not yet important, so the measured values of N_v/N_{v-1} can be equated to rate-constant ratios, k_v/k_{v-1} . The experimentally determined ratios $N_3/N_2 \geq 0.83$ for DF and $N_2/N_1 \geq 1.0$ for HF indicate that Reaction (2) gives DF($v=3$) and HF($v=2$) with quite high probability. In fact, if the

simple situation $k_3/k_2 = k_2/k_1 = k_1/k_0$ exists (we have no evidence of this), then 18% of the DF molecules are born in the $v=3$ state and one-third of the reaction heat is initially placed in vibrational states $v=3, 2, 1$.

Most important, probably, is that this chemical laser presents a much simpler interpretive problem than that of the H₂-Cl₂ laser. The system is under better control in many respects and its high gain facilitates study. We believe the rate-constant ratios reported here can be measured more reliably still and such experiments will be conducted. Furthermore, we are pursuing means of measuring the HF k_1/k_0 ratio and the DF k_2/k_1 and k_1/k_0 ratios to give a complete picture. Thus, the UF₆-H₂ system at last begins to yield the unique type of information that was anticipated in the earliest discussions of chemical lasers.

ACKNOWLEDGMENTS

This work was supported by the U. S. Air Force Office of Scientific Research. One of us (K.L.K.) thanks the Harkness Fellowships of the Commonwealth Fund for fellowship support.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 49, NUMBER 10 15 NOVEMBER 1968

Spectroscopy of K₂ Using Laser-Induced Fluorescence*

WILLIAM J. TANGO,† JOHN K. LINK,‡ AND RICHARD N. ZARE§

Joint Institute for Laboratory Astrophysics, Boulder, Colorado

(Received 21 May 1968)

When potassium vapor contained in a cell of aluminosilicate glass at 300°C is irradiated with the 6328-Å line of the He-Ne laser, several fluorescence series are excited which originate from the $B^1\Pi_u$ state of the $^{39}\text{K}_2$ molecule. Analysis of the fluorescence allows the spectroscopic constants (cm^{-1}) of the $X^1\Sigma_g^+$ ground state as measured by Loomis and Nusbau to be corrected, giving

$$\begin{aligned} \omega_e &= 92.021, & B_e &= 0.056743, \\ \omega_e x_e &= 2.829 \times 10^{-1}, & \alpha_e &= 1.65 \times 10^{-4}, \\ \omega_e y_e &= -2.055 \times 10^{-8}, & \gamma_e &= -7.2 \times 10^{-6}, \\ D_e &= 8.63 \times 10^{-8}, & \delta_e &= +1.5 \times 10^{-7}. \end{aligned}$$

The laser line is found to coincide with several molecular transitions. Three of these were determined from analysis of the spectrum to be ($v''=0, J''=82$) \rightarrow ($v'=7, J'=81$), ($v''=0, J''=18$) \rightarrow ($v'=6, J'=17$), and ($v''=1, J''=72$) \rightarrow ($v'=8, J'=72$). Radiation from K atoms accompanying K₂ excitation is also observed. It is proposed that the mechanism primarily responsible for the atomic potassium emission is the excitation transfer reaction $\text{K}_2^* + \text{K} \rightarrow \text{K}_2 + \text{K}^*$, leaving the K₂ molecule vibrationally excited.

I. INTRODUCTION

Development of intense, highly monochromatic lasers has opened the possibility of exploiting their use as light sources in photochemistry, molecular spectroscopy, and energy-transfer studies. Within the

* This work was supported by the National Science Foundation, the U.S. Atomic Energy Commission, and the Advanced Research Projects Agency (Project DEFENDER), monitored by the U.S. Army Research Office, Durham, under Contract DA-31-124-ARO-D-139.

† National Science Foundation Predoctoral Fellow.

‡ Joint Institute for Laboratory Astrophysics Postdoctoral Research Associate, 1966-1967. Present address: Department of Psychology, University of Colorado, Boulder, Colorado 80302.

§ Alfred P. Sloan Research Fellow.

past year a number of promising experiments¹⁻⁵ have been undertaken using the capability of the laser to

¹ (a) L. O. Hocker, M. A. Kovacs, C. K. Rhodes, G. W. Flynn, and A. Javan, Phys. Rev. Letters **17**, 233 (1966); (b) W. B. Tiffany, H. W. Moos, and A. L. Schawlow, Science **157**, 40 (1967). The latter paper also gives a number of references to earlier work in the field.

² J. R. Novak and M. W. Windsor, J. Chem. Phys. **47**, 3075 (1967).

³ K. G. P. Sulzmann, F. Bien, and S. S. Penner, J. Quant. Spectry. Radiative Transfer **7**, 969 (1967).

⁴ A. M. Ronn and D. R. Lide, J. Chem. Phys. **47**, 3668 (1967); A. M. Ronn, *ibid.* **48**, 511 (1968).

⁵ J. T. Yardley and C. B. Moore, J. Chem. Phys. **45**, 1066 (1967); C. B. Moore, R. E. Wood, B. Hu, and J. T. Yardley, *ibid.* **45**, 4222 (1967); J. T. Yardley and C. B. Moore, *ibid.* **48**, 14 (1968).

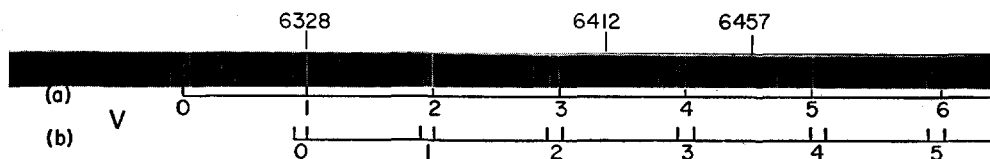


FIG. 1. The fluorescence spectrum of K₂ in the region of the exciting 6328-Å laser line: (a) the fluorescence series arising from the Q-branch transition ($v''=1, J''=72$) \rightarrow ($v'=8, J'=72$); (b) the fluorescence series resulting from the transition (0, 82) \rightarrow (7, 81).

excite individual states of molecules, and the opportunity exists for substantial gains in these fields. In particular, we have recently described experiments in which the 6328-Å He-Ne laser line was used to excite selectively potassium molecules electronically, allowing us to observe their subsequent fluorescence.⁶ Since then, molecular fluorescence using an argon-ion laser as a light source has been reported for I₂ by Ezekiel and Weiss⁷ and for Rb₂ and Cs₂ by McClintock and Balling.⁸ These findings encourage us to believe that laser-induced fluorescence studies are of widespread applicability.

Diatomic molecules like K₂, with large moments of inertia and small force constants, exhibit absorption spectra which are exceedingly complex and difficult to interpret. This has limited the study of these molecules, although they are of theoretical and experimental interest. The emission spectrum of a molecule, in the absence of collisions, excited by a single narrow line overlapping one or more absorption lines, is termed resonance fluorescence. Because the emitting levels are precisely and only those populated by the excitation line, resonance fluorescence is often much easier to analyze than the corresponding absorption spectrum.⁹ Laser excitation is a particularly advantageous means of producing resonance fluorescence since a significant number of molecules can be prepared in specific rotational-vibrational levels of the excited electronic state. This then facilitates the gathering of information about these states and the monitoring of subsequent energy-transfer processes they may undergo.

II. EXPERIMENTAL CONDITIONS

In the case of K₂, with a Doppler width of 0.03 cm⁻¹ at 600°K, it was found that the 6328-Å line from a multimode He-Ne laser (which has a 0.05-cm⁻¹ line-width) excited at least five rotational-vibrational levels of the B ¹Π_u state, and probably several times that number in total. The potassium vapor, in equilibrium with liquid potassium metal, was contained in a T-shaped cell of Corning 1720 aluminosilicate glass at 300°C. Approximately 0.5% of the vapor is in the form of K₂ at this temperature.¹⁰ The cell remained reasonably transparent for tens of hours at temperatures up to

⁶ W. J. Tango, J. K. Link, and R. N. Zare, *Bull. Am. Phys. Soc.* **12**, 1147 (1967); **13**, 847 (1968).

⁷ S. Ezekiel and R. Weiss, *Phys. Rev. Letters* **20**, 91 (1968).

⁸ R. M. McClintock and L. C. Balling, *Bull. Am. Phys. Soc.* **13**, 55 (1968).

⁹ R. D. Verma, *J. Chem. Phys.* **32**, 738 (1960).

¹⁰ M. Lapp and L. P. Harris, *J. Quant. Spectry. Radiative Transfer* **6**, 169 (1966).

390°C; under these conditions Pyrex or quartz cells rapidly become opaque due to attack by the potassium. The laser used for excitation was a 50-mW He-Ne laser having 17 axial modes with a mode spacing of 83 MHz at 6328 Å.¹¹

The fluorescence was photographed in the region 6000–7500 Å using the Berkeley 21-ft concave grating with a Paschen mount which has a first-order dispersion of 1.3 Å/mm and a resolution of roughly 10⁶. Exposures varying from 20 min to 2 h with 20-μ slits were made on Kodak IIA-F and I-N (hypersensitized) plates. Figure 1 shows one of the plates in the region of the exciting laser line. The thorium spectrum was used as a wavelength calibration standard and line positions were measured with a microdensitometer comparator. A computer program¹² was then used to calculate the dispersion of the photographic plate and to generate a list of vacuum wavenumbers with a relative accuracy of ±0.03 cm⁻¹ for the observed lines.

III. SPECTROSCOPIC ANALYSIS

The fluorescence arising from a given excited state of K₂ consists of a series of single lines (Q series) if $\Delta J=0$ on absorption, or of doublets (P and R series) if $\Delta J=\pm 1$ for the exciting transition.¹³ The observed fluorescence spectrum (Fig. 1) is seen to consist of very many of these series superimposed on each other; each one originates from a different rotational-vibrational level of the ¹Π_u state. The actual line positions $\nu(v'', J''; v', J')$ can be calculated from the energy level differences of a nonrigid symmetric top³:

$$\nu(v'', J''; v', J') = T_e + G(v') + F_{v'}(J) - G(v'') - F_{v''}(J), \quad (1)$$

where

$$F_v(J) = B_v[J(J+1) - \Omega^2] + D_v[J(J+1)]^2 \quad (2)$$

and

$$G(v) = \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + \omega_e y_e(v+1/2)^2 + \dots \quad (3)$$

Here T_e is the electronic term value (the separation

¹¹ We are grateful to the Spectra-Physics Corporation for making this laser available to us.

¹² We wish to express our thanks to Miss Helen Johansen for assisting us to use the Berkeley computer programs.

¹³ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Co., Inc., Princeton, N.J., 1950). The notation throughout this section conforms to that used by Herzberg.

between the minima of the two potential curves), Ω is the projection of the electronic angular momentum on the internuclear axis, v is the vibrational quantum number, and J is the total angular momentum of the molecule excluding nuclear spin. The rotational constant B_v equals

$$B_v - \alpha_e(v+1/2) + \gamma_e(v+1/2)^2 + \delta_e(v+1/2)^3 + \dots;$$

the centrifugal stretching constant D_v is well approximated by the formula $D_v = D_e = 4B_e^3/\omega_e^2$ [Eq. (III-118) of Ref. (13)]. The spacing between lines belonging to the same series and having vibrational and rotational quantum numbers (v'', J'') and $(v''-1, J'')$ is

$$\begin{aligned} \Delta\nu_{v''} = & \omega_e + \frac{1}{4}\omega_e\gamma_e - (\alpha_e - \frac{1}{4}\delta_e)J''(J''+1) \\ & - 2[\omega_e x_e - \gamma_e J''(J''+1)]v'' \\ & + 3[\omega_e y_e + \delta_e J''(J''+1)]v''^2 + \dots \quad (4) \end{aligned}$$

The spacing between the two doublet members of a P and R series is

$$\Delta\nu_{J'} = 4B_v(J'+1/2) - 6D_v(J'+1/2) - 8D_v(J'+1/2)^3. \quad (5)$$

In Eqs. (4) and (5) the spectroscopic constants ω_e , $\omega_e x_e$, etc., refer to the lower state and the double primes have been omitted for conciseness.

Since Q series, in contrast to P and R series, do not allow one to determine independently the rotational and vibrational quantum numbers, it is difficult to analyze them unless the spectroscopic constants are already known to high accuracy. For this reason the initial analysis was restricted to P and R series. If the vibrational numbering of the lines of two P and R series is known (this can be inferred from the number of anti-Stokes lines; i.e., the number of lines appearing to the blue side of the exciting line), the values of $\Delta\nu_{J'}$ can be plotted graphically against $(v''+1/2)$. For P and R series originating from small values of J' , the ratio of the intercepts at $v''+1/2=0$ will give the ratio of $(J'+1/2)$ for each series. Since J' is an integer, this will determine the two J' values to within a common factor. Continuing this process for several series will eventually give all the values of J' , and hence the spectroscopic constants. This technique, which requires no prior knowledge of the system, was not practical with the K_2 spectrum for two reasons. First, there were too few P and R series identified; and second, the smallness of B_v'' causes errors, due to inaccuracies in the line positions, to accumulate rapidly.

In the case of K_2 , we were fortunate to have the analysis of Loomis and Nusbaum¹⁴ on the absorption spectrum of K_2 . If the constants are already known approximately, accurate values can be found from two or more P and R series. An error in B_v'' will yield a

nonintegral value of J' when used in Eq. (5). This was done for a short P and R series, attributed to a $v''=0 \rightarrow v''=6$ transition, with an apparent " J' " of 17.8. By forcing J' to be 18, a preliminary value of B_e'' was obtained. This value was used to fit a long series (consisting of 18 doublets) to Eqs. (4) and (5). The actual line positions were also calculated by Eq. (1) adjusting all the constants, including T_e , to reproduce the observed spectrum. The series was identified as arising from the $(v''=0, J''=82) \rightarrow (v'=7, J'=81)$ transition.

TABLE I. A comparison of observed and calculated line positions (cm^{-1}) for the fluorescence series originating from the $(v'=7, J'=81)$ excited state. The calculated line positions have been computed using the constants of Table II.

v''	J''	ν_{obs}	ν_{calc}	$\nu_{\text{obs}} - \nu_{\text{calc}}$
0	80	15 816.14	15 816.13	0.01
	82	798.03	798.03	0.00
1	80	725.84	725.84	0.00
	82	707.84	707.80	0.04
2	80	636.24	636.22	0.02
	82	618.24	618.25	0.00
3	80	...	547.28	...
	82	...	529.37	...
4	80	458.99	459.01	-0.02
	82	441.16	441.17	-0.01
5	80	...	371.44	...
	82	...	353.67	...
6	80	284.59	284.56	0.03
	82	266.87	266.87	0.00
7	80	...	198.38	...
	82	...	180.77	...
8	80	112.93	112.91	0.02
	82	095.41	095.38	0.03
9	80	...	028.15	...
	82	...	010.71	...
10	80	14 944.04	14 944.12	-0.08
	82	926.71	926.76	-0.05
11	80	860.89	860.81	0.08
	82	843.62	843.54	0.08
12	80	...	778.24	...
	82	...	761.06	...
13	80	696.40	696.40	0.00
	82	679.30	679.31	-0.01
14	80	615.30	615.31	-0.01
	82	598.29	598.31	-0.02
15	80	... ^a	534.98	...
	82	518.05	518.07	-0.02
16	80	455.39	455.41	-0.02
	82	438.56	438.59	-0.03
17	80	376.61	376.60	0.01
	82	359.89	359.87	0.02
b				

^a This line occurred at the end of one of our plates and its wavelength could not be measured.

^b Two more doublet members were observed in this series, but their wavelengths were not measured.

¹⁴ F. W. Loomis and R. E. Nusbaum, Phys. Rev. **38**, 2153 (1931).

The observed and calculated line positions are shown in Table I; the constants used in fitting the data are given in Table II.¹⁵ In order to be certain that these constants could reproduce the other features of the spectrum, another series (a *Q* series) was analyzed. It agreed, within the errors of the line positions, with the fluorescence series caused by a (1, 72)→(8, 72) transition. We have not attempted to generate other expected fluorescence series, since the known errors in the upper-state constants prevent a unique identification.

The potential curves of the *X* and *B* states were constructed¹⁶ from the spectroscopic constants using the Rydberg–Klein–Rees method. These are shown in Fig. 2.

The Franck–Condon factors for the various vibrational transitions were computed from these curves and are compared with the observed intensities for one series in Fig. 3. The agreement between the observed

TABLE II. Spectroscopic constants for the $X^1\Sigma_g^+$ state of $^{39}\text{K}_2$ in cm^{-1} . The average deviation of lines computed with these constants is about 0.03 cm^{-1} .

ω_e	92.021
$\omega_e x_e$	2.829×10^{-1}
$\omega_e y_e$	-2.055×10^{-3}
B_e	0.056743
α_e	1.65×10^{-4}
γ_e	-7.2×10^{-6}
δ_e	1.5×10^{-7}
D_e	8.63×10^{-8}
$T_e(^1\Pi_u)$	15 376.74

and calculated intensities provides an additional check on the proposed vibrational assignments, although no confirmation of the rotational assignments is possible since the Franck–Condon factors are too insensitive to the rotational state. For the ground state, $r_e'' = 3.905 \text{ \AA}$, and for the upper state, $r_e' = 4.212 \text{ \AA}$. The internuclear separations are unusually large compared with typical strongly bound diatomic molecules. The relatively large difference of 0.307 \AA between r_e'' and r_e' explains in part the existence of the extended fluorescence series that are observed. The dissociation energy D_e of the *X* state was estimated by a Birge–Spencer extrapolation¹⁷ to be 4516 cm^{-1} (0.56 eV); dissociation appears to occur at a v'' of about 84. Since the highest v'' observed was around 20, we cannot be certain of the error in D_e , but our estimate is probably high. This value

¹⁵ The upper-state constants B_e' and D_e' were recalculated using Loomis and Nusbaum's result,¹⁴ $B_e'' - B_e' = 0.00798$, giving a value for $B_e' = 0.048763 \text{ cm}^{-1}$ and $D_e' = 8.25 \times 10^{-8} \text{ cm}^{-1}$.

¹⁶ R. N. Zare, *J. Chem. Phys.* **46**, 1934 (1964); Univ. Calif. Radiation Lab. Rept. UCRL-10925, 1963.

¹⁷ R. T. Birge and H. Spomer, *Phys. Rev.* **28**, 259 (1926).

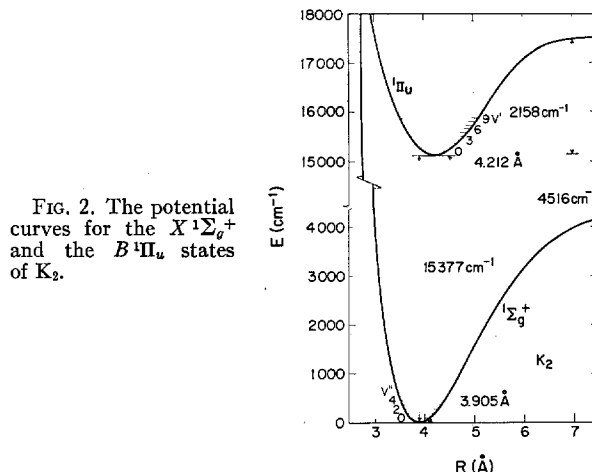


FIG. 2. The potential curves for the $X^1\Sigma_g^+$ and the $B^1\Pi_u$ states of K_2 .

is in fair agreement with spectroscopic¹⁸ and thermodynamic¹⁹ measurements. The potential maximum in the *B* state which was predicted to exist by King and Van Vleck²⁰ would thus seem to be quite small.

IV. ELECTRONIC ENERGY-TRANSFER PROCESSES

The technique of laser excitation of molecules also commends itself for energy-transfer studies. In Fig. 4 (upper portion) we show a spectrogram of the emission from a potassium vapor cell in the region of the first resonance lines of potassium ($\lambda = 7665$ and 7699 \AA) when the cell is irradiated with the 6328-\AA He–Ne laser line. For purposes of comparison, the lower portion of Fig. 4 shows the potassium resonance lines from a commercial potassium lamp. The atom density of around 1 torr results in a mean free path of 10^{-4} mm for line-center photons, explaining the diffuse, self-reversed character of the radiation.

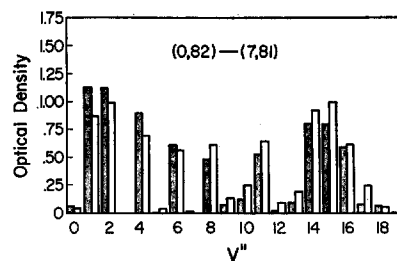


FIG. 3. A comparison of the observed and calculated intensities for the (0, 82)→(7, 81) transition. The shaded bars are the observed intensities measured by a microdensitometer and corrected for the plate spectral response; the open bars are the computed intensities scaled to fit on the graph.

¹⁸ F. W. Loomis and R. E. Nusbaum, *Phys. Rev.* **39**, 89 (1932) and R. E. Nusbaum and F. W. Loomis, *ibid.* **39**, 178 (1932) give $D_0 = 0.51 \pm 0.02 \text{ eV}$.

¹⁹ C. Lewis, *Z. Physik* **69**, 786 (1931), as corrected by Loomis and Nusbaum,¹⁸ found $D_0 = 0.56 \pm 0.04 \text{ eV}$.

²⁰ G. W. King and J. H. Van Vleck, *Phys. Rev.* **55**, 1165 (1949).

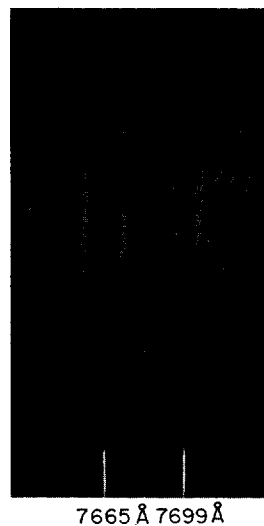
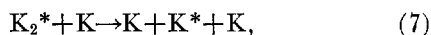


FIG. 4. Emission from the K_2 fluorescence cell in the neighborhood of the K-atom resonance lines. The upper portion of the spectrogram is a 20-min exposure of the fluorescence cell made by a 0.75-m focal length spectrograph with 30- μ slits on Polaroid 413 red-sensitive film. The lower part shows the potassium-atom resonance lines obtained from a standard Osram lamp.

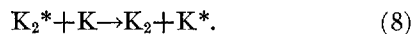
Several kinetic pathways suggest themselves as possible sources of the atomic emission: direct photodissociation of K_2 by the laser,



collisional breakup of the excited molecule due to collisions with atoms,



and "molecule-atom electronic energy exchange,"



We believe that (8) is the most likely explanation of the atomic emission. Processes (6) and (7) cannot be ruled out, but they might be expected to contribute a smaller fraction of the observed atomic radiation for several reasons. Based on energy considerations (see Fig. 2), direct dissociation can only occur from ground-state molecules which are highly vibrationally excited $v'' \gtrsim 15$. Not only are such states sparsely populated, but the poor vibrational overlap with the continuum states reduces the probability of direct dissociation. For the collisional break-up mechanism to be an effective process, the excited K_2^* molecules must be formed in a vibrational state which lies within kT of the $B^1\Pi_u$ dissociation limit. Once again, population and Franck-Condon-factor considerations argue against this process. The question arises whether multiple collisions may be responsible. The radiative lifetime of the $B^1\Pi_u$ state acts as an "internal clock" limiting the average number

of collisions an excited molecule can undergo. Preliminary measurements²¹ indicate that the K_2^* lifetime is much shorter than the 28-nsec lifetime of the 2P states of the potassium atom.²² Thus, at the pressures we used, multiple collisions are improbable. Molecule-atom electronic energy transfer is also limited by the radiative lifetime; however, the energy requirements and Franck-Condon-factor considerations appear quite favorable. Since the ground-state vibrational spacing of K_2 is about 90 cm^{-1} , the energy defect of (8) can be made much less than kT . It may be expected then that the nearly resonant process (8) is quite efficient for energy transfer.

If the K^* emission accompanying K_2 excitation is due to (8), it would be, to our knowledge, the first instance of molecule-atom electronic excitation transfer. McClintock and Balling⁸ have also reported seeing atomic emission upon laser excitation of alkali dimers. Perhaps molecule-atom excitation transfer can explain in part their observations as well. It is intriguing to speculate on the detailed mechanism of this excitation transfer process. One possibility is that (8) proceeds via atom-atom interchange,²³ in which the colliding K atom replaces another K atom in the molecule, "knocking out" an excited K^* atom. Alternatively (8) might proceed through direct excitation transfer in which the incoming atom interacts with the K_2^* molecule on the K_3^* potential surface, and departs in an excited state. Studies of electronic energy transfer in mixed alkali systems might lead to a resolution of this question.

ACKNOWLEDGMENTS

We are happy to acknowledge the support of the Associated Western Universities, which enabled two of us (W.J.T. and R.N.Z.) to travel to Berkeley to do this work. Our stay at the University of California was made more pleasant by the kind assistance of Professor Leo Brewer and Professor Sumner Davis, who made the facilities of the University and the Lawrence Radiation Laboratory available to us. We are also indebted to Richard T. Weppner of the Joint Institute for Laboratory Astrophysics for suggesting the use of aluminosilicate cells and for so ably constructing them.

²¹ We are grateful to P. T. Cunningham and Dr. R. Wolff at the University of California, Berkeley, for making these measurements.

²² J. K. Link, *J. Opt. Soc. Am.* **56**, 1195 (1966).

²³ Evidence for such atom-atom interchange processes has been provided by the recent crossed-beam chemiluminescent studies of M. C. Moulton and D. R. Herschbach, *J. Chem. Phys.* **44**, 3010 (1966).