The NaLi electronic ground state studied by laser induced fluorescence and Fourier transform spectroscopy

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PRELIMINARY COMMUNICATION

The NaLi electronic ground state studied by laser induced fluorescence and Fourier transform spectroscopy

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The $X\,^1\Sigma^+$ ground electronic state of the NaLi molecule has been studied by laser induced fluorescence recorded by a Fourier transform spectrometer. Ground state molecular constants and the derived rotationless potential energy curve up to $v'' = 20$ are reported. Improvements made in the heating system of the heat-pipe oven in order to produce NaLi molecules are also described. Comparison with previous work, theoretical and experimental, is made.

1. Introduction

The lightest alkali heteronuclear diatomic molecule, NaLi, has been the subject of a number of theoretical studies [1–10]. However, relatively few experimental results are available to date. Using the LIF technique, Hessel [11] was the first to observe the Na⁷Li spectrum. He excited a mixture of sodium and lithium in a heat-pipe oven [12] with 496·5 nm Ar⁺ laser line, and assigned series of P, R doublets and Q lines as due to a $^1\Pi$–$^1\Sigma$ transition. Fluorescence lines to the ground state vibrational levels

$$0 \leqslant v'' \leqslant 8$$

were reported and the first set of molecular constants for the ground state of NaLi was determined.

Several studies of the NaLi molecule have been made since Hessel's work. The first of these, by Dagdigian et al. [13], measures the polarizabilities of NaLi in the $(J = 1, M = 0)$ and $(J = 2, M = 0)$ rotational states of the $^1\Sigma^+$ ground-state using a supersonic molecular beam with an electric quadrupole state selector. From these measurements the molecular electric dipole moment ($\mu_0 = 0\cdot47 \pm 0\cdot03$ D) and the molecular polarizability ($\alpha_s = 43 \pm 5$ Å^3) were determined. Brooks et al. [14] observed nuclear resonance for ⁷Li in NaLi and reported a value of eqQ/h (⁷Li in NaLi) = 54 ± 5 kHz. Improved values for the molecular electric dipole moment and molecular polarizability have been given by Graff et al. [15]; they found $\mu_0 = \mu_0 = 0\cdot4463 \pm 0\cdot002$ D and $\alpha_s = 40 \pm 5$ Å^3. The ground state vibronic Stark coefficient $\mu_0^2/B_0 = 2740 \pm 5$ Å^3 was also determined. In this work a value of $eqQ/h = 28 \pm 4$ kHz, very different from that obtained by Brooks et al. [14], is given.
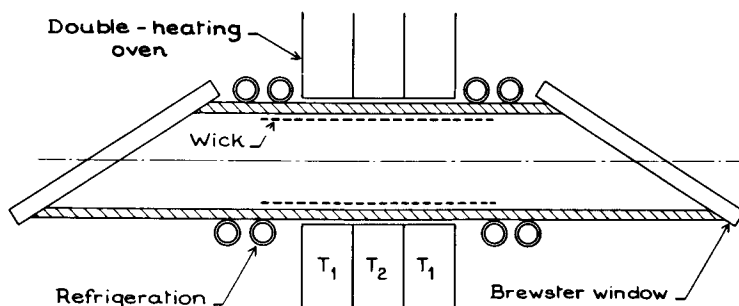
Figure 1. Heat-pipe with double-heating oven. $T_1 = 500°C$, $T_2 = 600°C$. Internal diameter of the heat-pipe = 30 mm; wick length = 300 mm.

In an attempt to analyse collision-induced rotational transitions in electronically excited NaLi, Ottinger [16] recorded laser-induced fluorescence spectra and observed that, due to the greater number of allowed transitions as compared with Na_2 and Li_2, there were more cases of transitions with $+\Delta J$ and $-\Delta J$ having greatly different cross-sections ($+/-$ asymmetry or propensity of cross-sections) than in the homonuclear diatomic molecules. Later Zmbov *et al.* [17] determined the dissociation energy for the $X\,^1\Sigma^+$ electronic ground-state ($D_0'' = 86.6 \pm 6$ kJ mol^{-1}), and the ionization potential of 4.94 ± 0.10 eV, in a mass spectrometric study. In all of these experiments Hessel's molecular constants and assignments were used.

The first attempt to obtain new spectroscopic constants was made by Engelke *et al.* [18]. Using an injection heat-pipe and a molecular beam to produce NaLi molecules, LIF spectra were obtained after excitation with a dye laser and Ar$^+$ laser lines. However, the r.m.s. error of the fit equal to 0.18 cm^{-1}, was rather large compared to the quoted absolute uncertainty in the measurements of ± 0.05 cm^{-1} for unblended lines and ± 0.03 cm^{-1} in relative positions.

In the present work, we have reinvestigated the fluorescence of the NaLi molecule induced by Ar$^+$ and Kr$^+$ laser lines, because of the numerous inconsistencies found in previous studies.

2. Experimental

A standard heat-pipe [12] was used to produce NaLi molecules. Nearly equal parts of Na and Li were inserted in the heat-pipe, with argon as buffer gas. To produce sufficient lithium vapour, a temperature near 600°C is required. At this temperature, the sodium vapour pressure is of the order of 10 mbar [19]. As a result sodium atoms escape from the heated region, and condense at the cold extremities of the heat-pipe without producing NaLi. To overcome this problem a double heated oven has been constructed, as shown in figure 1. This oven which envelops the central part of the heat-pipe, can be divided in two regions:

(i) The middle section, which operates at a temperature of 600°C to optimize the production of lithium vapour.

(ii) The two outer sections, which are maintained at 500°C to ensure that the sodium vapour pressure is equal to the buffer gas pressure in the outermost part of the heat-pipe.

With this modification sodium can melt and wet the wick, evaporate, diffuse to the extremities and condense. The condensate returns through the wick back to the less heated portion of the tube, by capillary action. The same cycle is maintained for the lithium in the central part of the heat-pipe. Finally an equilibrium is reached for each heating section of the oven, and both lithium and sodium metal vapours fill the centre and end parts respectively.

In this way sodium and lithium vapours coexist and NaLi production is ensured. The double heating system is very stable and gives the possibility of working several hours (more than 15 hours) without refilling the heat-pipe. Two heat-pipes were constructed and filled with ^{23}Na, ^{7}Li and ^{23}Na, ^{6}Li respectively.

The laser beam was focused near the centre of the heat-pipe, and the backward fluorescence was imaged on to the entrance iris of a 2 m maximum path-difference Fourier transform spectrometer. An Ar$^+$ laser (Spectra-Physics 171-19) and a Kr$^+$ laser (Coherent Radiation K-3000) were used in the optical pumping of the NaLi molecule. A total of eight laser lines has been used, all of them running in multi-mode conditions. The recorded fluorescence covers a region of 10 000 cm^{-1} around the laser line with a resolution limit ranging from 0·028 cm^{-1} to 0·046 cm^{-1} for different recordings. The uncertainties for wavelength measurements vary from 0·005 cm^{-1} for the strongest lines, to 0·020 cm^{-1} for the weakest ones.

Doublets (P, R lines) and singlets (Q lines) are observed when optical pumping is made by the Ar$^+$ lines, transitions issued from the $B\,^1\Pi$ state as suggested by Engelke *et al.* [18]. Only doublet series were observed when pumping with red Kr$^+$ lines, coming from the lowest singlet excited $A\,^1\Sigma^+$ state.

3. Observations

The NaLi appears simultaneously with Na$_2$ and Li$_2$, a fact that complicates the analysis of the spectrum. This difficulty was overcome by comparing the recorded spectra with the fluorescence spectra of 'pure' Na$_2$ or Li$_2$ induced by the same wavelengths.

For nearly all the observed spectra, the doublets (P and R lines) and singlets (Q lines) show collision induced satellite lines, giving additional rotational information for each v''-progression. Figure 2 depicts a typical spectrum consisting of a series of P, R doublets, coming from the $A\,^1\Sigma^+ \rightarrow X\,^1\Sigma^+$ transition. From figure 2 it can be noted that the rotational relaxation lines are all smoothly positioned, without any noticeable perturbation. However the doublet with $J' = 19$ seems to be absent or to have a strongly decreased intensity. An accidental predissociation is possibly responsible for this phenomenon which has so far been thoroughly studied only in Li$_2$ [20–22].

4. Analysis and discussion

With the existing molecular constants for the NaLi ground state reported by Engelke *et al.* [18], a tentative assignment of the transitions was made. However, not all the observed transitions could be simultaneously assigned with these reported constants.
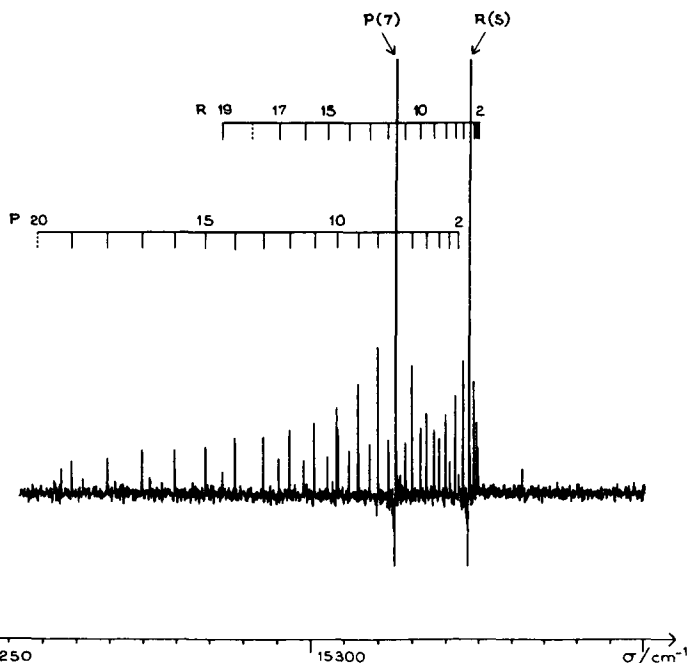
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Figure 2.   Part of a Na^{6}Li spectrum ($v'' = 0$) excited by the Kr$^+$ 676·4 mm laser line. The J'' identification of the P-lines and R-lines is given in the top. The true intensity ratio $I_{P(7)}/I_{P(8)} = 5$. Note that the lines $P(20)$ and $R(18)$ are missing. The lines that are not assigned are due to Na$_2$.

The improved molecular constants were obtained by a least-squares fit of the spacings Δv_{vib} and Δv_{rot} to the Dunham expression

$$E(v_i'', J_i'') - E(v_m'', J_m'') = \sum_{i, j} Y_{ij}'' \{ [\rho(v_i'' + 1/2)]^i [\rho^2 J_i''(J_i'' + 1)]^j$$

$$- [\rho(v_m'' + 1/2)]^i [\rho^2(J_m''(J_m'' + 1)]^j \}, \quad (1)$$

where

$$\Delta_{\mathrm{vib}} = E(v'' + 1, J'') - E(v'', J'')$$

and

$$\Delta_{\mathrm{rot}} = E(v'', J'' + 1) - E(v'', J'').$$

Wavenumbers for both isotopic species were simultaneously reduced using equation (1) and taking into account that $\rho = 1 \cdot 0$ for the Na^{7}Li and $\rho = 1 \cdot 06183215$ for Na^{6}Li. Assignments were changed until a minimum r.m.s. error was found. A total of 870 lines issued from 42 Q and 60 R, P-series were assigned to obtain the coefficients given in table 1. The r.m.s. error is equal to $3 \cdot 5 \times 10^{-3}$ cm^{-1}. The strongest observed transitions are reported in table 2. Considering that in the performed fit, equation (1), only the electronic ground state is taken into account, no vibrational quantum number has yet been assigned for the excited state. A centrifugal distortion constant equal to $0 \cdot 3227 \times 10^{-5}$ cm^{-1} is obtained using Kratzer's relation

$$Y_{02} = -4Y_{01}^3/Y_{10}^2.$$

Table 1. Dunham type coefficients for the $X\,^1\Sigma^+$ ground-state of Na^7Li and their standard deviations (all values in cm^{-1}).

Coeff.	Y_{ij}	σ
Y_{10}	$256 \cdot 54122$	$0 \cdot 19006 \times 10^{-2}$
Y_{20}	$-1 \cdot 6227115$	$0 \cdot 96025 \times 10^{-3}$
Y_{30}	$-4 \cdot 9465113 \times 10^{-3}$	$0 \cdot 22419 \times 10^{-3}$
Y_{40}	$1 \cdot 2470034 \times 10^{-4}$	$0 \cdot 28587 \times 10^{-4}$
Y_{50}	$-2 \cdot 3915599 \times 10^{-5}$	$0 \cdot 21568 \times 10^{-5}$
Y_{60}	$1 \cdot 2624541 \times 10^{-6}$	$0 \cdot 98439 \times 10^{-7}$
Y_{70}	$-3 \cdot 9886502 \times 10^{-8}$	$0 \cdot 26442 \times 10^{-8}$
Y_{80}	$6 \cdot 3418319 \times 10^{-10}$	$0 \cdot 38029 \times 10^{-10}$
Y_{90}	$-4 \cdot 0195071 \times 10^{-12}$	$0 \cdot 22353 \times 10^{-12}$
Y_{01}	$3 \cdot 7586202 \times 10^{-1}$	$0 \cdot 88725 \times 10^{-5}$
Y_{11}	$-3 \cdot 1465470 \times 10^{-3}$	$0 \cdot 14800 \times 10^{-5}$
Y_{21}	$-1 \cdot 0609573 \times 10^{-5}$	$0 \cdot 51644 \times 10^{-6}$
Y_{31}	$-1 \cdot 9034405 \times 10^{-6}$	$0 \cdot 92101 \times 10^{-7}$
Y_{41}	$1 \cdot 4678661 \times 10^{-7}$	$0 \cdot 83716 \times 10^{-8}$
Y_{51}	$-8 \cdot 5661080 \times 10^{-9}$	$0 \cdot 40228 \times 10^{-9}$
Y_{61}	$2 \cdot 2416889 \times 10^{-10}$	$0 \cdot 96709 \times 10^{-11}$
Y_{71}	$-2 \cdot 4852422 \times 10^{-12}$	$0 \cdot 90602 \times 10^{-13}$
Y_{02}	$-3 \cdot 2322192 \times 10^{-6}$	$0 \cdot 54755 \times 10^{-8}$
Y_{12}	$-1 \cdot 4703704 \times 10^{-8}$	$0 \cdot 60636 \times 10^{-9}$
Y_{22}	$-1 \cdot 1660844 \times 10^{-9}$	$0 \cdot 32318 \times 10^{-10}$
Y_{03}	$3 \cdot 0139021 \times 10^{-11}$	$0 \cdot 95458 \times 10^{-12}$
Y_{13}	$-2 \cdot 2912316 \times 10^{-12}$	$0 \cdot 14749 \times 10^{-12}$
Y_{23}	$3 \cdot 1586132 \times 10^{-13}$	$0 \cdot 95468 \times 10^{-14}$
Y_{33}	$-1 \cdot 3377970 \times 10^{-14}$	$0 \cdot 22829 \times 10^{-15}$

Table 2. Strongest transitions excited by Ar^+ and Kr^+ laser lines in Na^7Li and Na^6Li.

Laser line/nm		v'' range observed	Species
$752 \cdot 5$	$R(61)$	0–16	Na^7Li
$676 \cdot 4$	$R(55)$	0–15	Na^7Li
	$P(7)$	0–16	Na^6Li
$514 \cdot 5$	$R(16)$	0–8	Na^6Li
	$Q(11)$	0–8	Na^6Li
$501 \cdot 7$	$Q(21)$	0–9	Na^6Li
	$Q(29)$	0–6	Na^6Li
	$P(10)$	0–14	Na^7Li
	$P(9)$	0–13	Na^7Li
	$R(25)$	0–9	Na^6Li
$496 \cdot 5$	$P(30)$	0–10	Na^7Li
$488 \cdot 0$	$Q(28)$	3–26	Na^6Li
	$Q(48)$	1–26	Na^6Li
$476 \cdot 5$	$Q(37)$	1–40	Na^7Li
$476 \cdot 2$	$Q(20)$	0–22	Na^6Li

Table 3. Vibrational term values G_v, turning points R_{min} and R_{max}, obtained from IPA calculations based on the molecular constants of table 1 (R_{min} and R_{max} in Å).

v	G_v/cm^{-1}	R_{min}	R_{max}
0	127·806	2·7402	3·0537
1	384·079	2·6406	3·1866
2	631·066	2·5762	3·2849
3	877·738	2·5262	3·3694
4	1121·065	2·4846	3·4463
5	1361·015	2·4487	3·5180
6	1597·551	2·4169	3·5863
7	1830·631	2·3884	3·6522
8	2060·212	2·3624	3·7162
9	2286·245	2·3385	3·7789
10	2508·676	2·3164	3·8407
11	2727·449	2·2959	3·9019
12	2942·503	2·2766	3·9627
13	3153·772	2·2585	4·0234
14	3361·187	2·2415	4·0842
15	3564·674	2·2255	4·1452
16	3764·152	2·2103	4·2067
17	3959·535	2·1959	4·2688
18	4150·728	2·1824	4·3318
19	4337·633	2·1695	4·3959
20	4520·143	2·1573	4·4612

This value differs only by 0·17 per cent from the reported Y_{02} in table 1. By the Pekeris relation

$$Y_{11} = 6Y_{01}^2[1 - (-Y_{20}/Y_{01})^{1/2}]/Y_{10}$$

a value of $-0·3567 \times 10^{-2}$ cm^{-1} is calculated, differing by 15 per cent from the Y_{11} obtained in the fit and given in table 1. A value that lies between the percental error for the calculated Y_{11} from the constants of Hessel and Vidal [23], and Kusch and Hessel [24], for Li$_2$ and Na$_2$, respectively.

An IPA potential (inverted perturbation approach) energy curve was calculated using the Y_{ij} coefficients obtained in this work [25]. The energy values and turning points are given in table 3. It should be noted that one Q-series with a J-value equal to 37 has been assigned going up to $v'' = 40$. But being the only series that goes to such high vibrational quantum numbers we think that there is not presently sufficient experimental data to calculate a reliable potential energy curve up to $v'' = 40$. Nevertheless, the line wavenumbers of this series up to $v'' = 40$ were introduced in the data reduction giving the constants quoted in table 1.

Table 4. Comparison between spectroscopic constants for Na^{7}Li from previous and present work. All values in cm^{-1}, except R_e in Å.

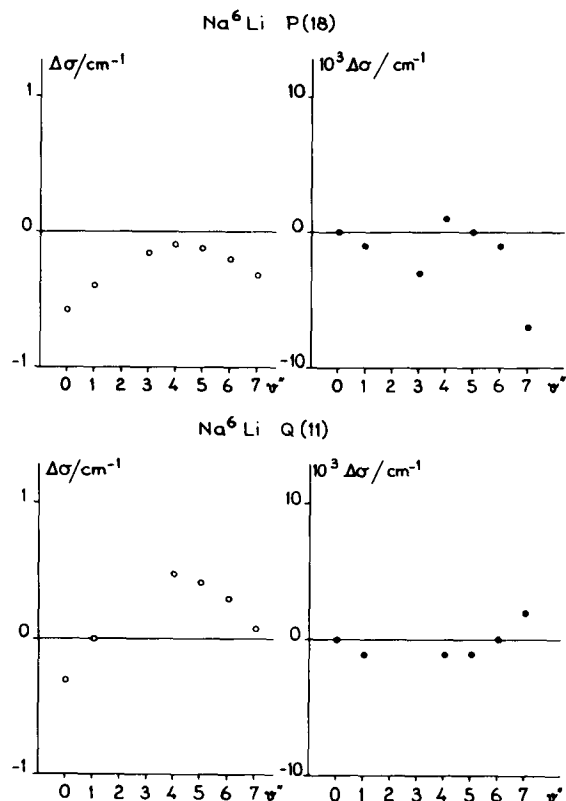| Ref.	ω_e	$\omega_e x_e$	B_e	α_e	R_e
[10]	256·80	1·608	0·3758	0·00313	2·890
[18]	256·99 (8)	1·657 (13)	0·3768 (15)	0·00381 (8)	2·885 (6)
Present work	256·54 (1)	1·622 (7)	0·3758 (6)	0·00314 (6)	2·889 (2)

Na^{6}Li P(18)

Na^{6}Li Q(11)

Figure 3. Differences between our observed wavenumbers and recalculated wavenumbers using Engelke *et al.* [18] constants (left), and our observed and recalculated wavenumbers (right), for the identically assigned series, P(18) and Q(11), pumped by Ar$^+$ 514·5 nm. It should be noted that the left vertical scale is 100 times greater than the right vertical scale. ●, present work; ○ [18]. The $v'' = 3$ transition in the Q(11) series is the laser line and for this reason is not recalculated.

Comparing our results with the theoretical [10] and experimental results [18], it can be noted that they are in reasonably good agreement with both of them (table 4). However, 'reasonably good' can mean departures reaching two orders of magnitude from our results as shown below.

Some comments should be made about the difference between our results and those of Engelke *et al.* [18]. In the present work all the assigned lines were fitted using equation (1). In this procedure the ground-state constants are not correlated with those of the upper state. The upper state being strongly perturbed, this kind of fit is better than one in which the molecular constants of the upper state are floated, because series issued from perturbed state levels ought in this case to be omitted from the fit. In the work of Engelke *et al.* the constants were obtained by fitting the ground-state and the excited electronic state molecular constants simultaneously. This kind of procedure is liable to introduce errors for the reasons discussed above, and being correlated, the errors will be nearly the same for both states. This assumption can explain the fact that the Y_{i1} and Y_{i2} coefficients reported by Engelke *et al.* have errors of the same order of magnitude for both states.

Figure 3 shows the comparison first between the difference of our observed wavenumbers and those recalculated by Engelke *et al.* Y_{ij} constants, and second the difference of our observed and recalculated wavenumbers for the same series. It can be noted that the Y_{ij} constants set reported by Engelke *et al.* do not reproduce the observed wavenumbers within the FTS uncertainty.

5. Conclusions

The development of the double-heating combined with the standard heat-pipe oven has proved to be an easy and powerful tool for the production of NaLi molecules. With this source LIF spectra of NaLi are reinvestigated, and a new and improved set of Y_{ij} coefficients is reported, and the first observation, in high resolution spectroscopy, of the $A\,{}^1\Sigma^+ \to X\,{}^1\Sigma^+$, first observed by Kappes *et al.* [26], transition is analysed. Further studies of excited electronic states require a good knowledge of the $X\,{}^1\Sigma^+$ electronic ground state. This explains the spectroscopic reinvestigation presented in this work.

Measurements are currently in progress to obtain fluorescence spectra involving the higher bound vibrational levels in order to improve the value of the previously reported dissociation limit for the ground electronic state.

References

[1] BERTONCINI, P. J., DAS, G., and WAHL, A. C., 1970, *J. chem. Phys.*, **52**, 5112.
[2] GREEN, S., 1971, *J. chem. Phys.*, **54**, 827.
[3] ROSMUS, P., and MEYER, W., 1976, *J. chem. Phys.*, **65**, 492.
[4] ROACH, A. C., 1972, *J. molec. Spectrosc.*, **42**, 27.
[5] HABITZ, P., SCHWARZ, W. H. E., and AHLRICHS, R., 1977, *J. chem. Phys.*, **66**, 511.
[6] FRICKER, H. S., 1971, *J. chem. Phys.*, **55**, 5034.
[7] KONOWALOW, D. D., and ROSENKRANTZ, M. E., 1977, *Chem. Phys. Lett.*, **69**, 54.
[8] SHEPARD, R. S., JORDAN, K. D., and SIMONS, J., 1978, *J. chem. Phys.*, **69**, 1788.
[9] JONES, R. O., 1980, *J. chem. Phys.*, **72**, 3197.
[10] SCHMIDT-MINK, I., MÜLLER, W., and MEYER, W., 1984, *Chem. Phys. Lett.*, **112**, 120.
[11] HESSEL, M. M., 1971, *Phys. Rev. Lett.*, **26**, 215.
[12] VIDAL, C. R., and COOPER, J., 1969, *J. appl. Phys.*, **40**, 3370.
[13] DAGDIGIAN, P. J., GRAFF, J., and WHARTON, L., 1971, *J. chem. Phys.*, **55**, 4980.
[14] BROOKS, R. A., ANDERSON, C. H., and RAMSEY, N. F., 1972, *J. chem. Phys.*, **56**, 5193.
[15] GRAFF, J., DAGDIGIAN, P. J., and WHARTON, L., 1972, *J. chem. Phys.*, **57**, 710.
[16] OTTINGER, CH., 1973, *Chem. Phys.*, **1**, 161.
[17] ZMBOV, K. F., WU, C. H., and IHLE, H. R., 1977, *J. chem. Phys.*, **67**, 4603.
[18] ENGELKE, F., ENNEN, G., and MEIWES, K. H., 1982, *Chem. Phys.*, **66**, 391.
[19] NESMEYANOV, A. N., 1963, *Vapor Pressure of the Chemical Elements*, edited by R. Gary (Elsevier Publishing Company), pp. 122–137.
[20] XIE, X., and FIELD, R. W., 1985, *Chem. Phys.*, **90**, 337.
[21] RICE, S. F., XIE, X., and FIELD, R. W., 1986, *Chem. Phys.*, **104**, 161.
[22] SCHMIDT-MINK, I., and MEYER, W., 1985, *Chem. Phys. Lett.*, **121**, 49.
[23] HESSEL, M. M., and VIDAL, C. R., 1979, *J. chem. Phys.*, **70**, 4439.
[24] KUSCH, P., and HESSEL, M. M., 1978, *J. chem. Phys.*, **68**, 2591.
[25] VIDAL, C. R., and SCHEINGRABER, H., 1977, *J. molec. Spectrosc.*, **69**, 46.
[26] KAPPES, M. M., MARTI, K. O., RADI, P., SCHÄR, M., and SCHUMACHER, E., 1984, *Chem. Phys. Lett.*, **107**, 6.