

Fluorescence spectra of the NaI molecule

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The fluorescence excitation spectrum and fluorescence emission spectra of sodium iodide vapor are reported for the first time. The emission spectrum contains a $v'' = 0$ progression and $v'' = 1$ progression of a transition of the NaI molecule, as well as many other bands due to other species. The spectrum is taken from a seeded hypersonic nozzle beam excited by a tunable laser. A vibrational analysis is given, part of the upper state potential is constructed, and the results are related to photodissociation studies.

Sodium iodide is the only alkali halide whose vapor is known to have a banded absorption spectrum.¹⁻³ This spectrum has long been presumed without proof to be due to a bound-bound transition in the diatomic NaI molecule. Specifically it has been supposed to be due to the ${}^1\Sigma^+$ (or 0^+) $\rightarrow X^1\Sigma^+$ charge transfer transition from the ionic ground state to the first electronically excited state of the same symmetry type as the ground state. If this interpretation is correct, the bound character of the state arises from the avoided crossing of the ionic and neutral-atom potential curves that force the excited state to be like neutral atoms for internuclear distances significantly shorter than the crossing distance R_x of 6.930 Å and like an ion pair—and hence two ions attracted to one another—at distances significantly greater than the transition region around R_x .

Previous attempts to analyze this spectrum were plagued by its high density of lines. Several factors compound this difficulty. The high temperatures required to vaporize the salt cause several vibrational levels and many rotational levels of the X state to be populated, and the potential well of the excited state is both broad and displaced to internuclear distances larger than the ground state minimum. This makes the vertical Franck-Condon transitions from the ground state cover a broad range of energy of the upper state, and forces the density of vibration-rotation states in this energy range to be high. One of us⁴ and Berg and Skewes⁵ reported an apparent interval of about 35 cm^{-1} , but without assignment. Berg and Skewes find this interval in the regions ~ 415 – 450 and 423 – 432 nm. The matrix spectra of NaI^6 showed diffuse bands with frequency distances of 166, 141, and 129 cm^{-1} in solid Ar, N_2 , and Kr, respectively. Photodissociation experiments at fixed⁷⁻⁹ and variable^{10,11} frequencies indicate that both parallel and perpendicular transitions contribute to molecular dissociation at energies below the dissociation limit of the ionic potential curve.

We report here the first observation of the fluorescence excitation spectrum and of fluorescence emission spectra from cold sodium iodide vapor seeded in a hypersonic nozzle beam. Our results include the assignment of several bands of that excitation spectrum to the NaI molecule, and a vibrational analysis of the Franck-Condon region accessible from the ground and the first excited vibrational levels of the X state. The results permit us to infer the shape of a portion of the excited state potential curve and to estimate the separation of the ground and excited potential curves at the

crossing point. We also find that many of the bands of the excitation spectrum are due to species that are *not* monomeric NaI molecules.

EXPERIMENTAL

The experiments were conducted with the jet of alkali halide in carrier gas, usually He, along one horizontal axis, the laser beam along the perpendicular horizontal axis and the direction of observation of the emission along the vertical axis, from above for total emission to give the excitation spectrum or from below for dispersed fluorescence emission spectra. The salt source was a double oven operating in the range 670–710 K, with a piece of oxidized nickel wire and a bit of quartz wool in the two-phase chamber; the nickel served to be wet by the salt, and the wool filtered salt particles out of the helium carrier so that solid or liquid salt was kept out of the second chamber, where the exit nozzle was. The most effective nozzles were quartz with apertures of 50–100 μm , although stainless steel nozzles were also used. Two laser systems were used for different series of experiments. In both, a Nd:YAG pulsed laser (Quanta-Ray DCR-1) produced a beam that was first doubled in frequency and then used to pump a dye laser. In one laser system, the beam of the dye laser was preamplified and amplified in cells pumped by some of the 532 nm radiation from the doubler and then was redoubled to give ultraviolet radiation. In the second system, the radiation from the preamplified and amplified dye laser was mixed with 1064 nm infrared radiation from the Nd:YAG laser to give radiation in the very near ultraviolet. The range scanned in the excitation studies was $393.0 \geq \lambda \geq 318.0$ nm.

Emission was collected in some experiments with a Cassegrain telescope and in others, with a quartz doublet lens. The optics for collecting the dispersed fluorescence, essentially as designed by Sharfin¹² focused this radiation into a 1 m Spex monochromator.

RESULTS

The spectral region of the excitation spectrum begins at about 384.0 nm and extends to shorter wavelengths. At wavelengths shorter than 320.0 nm, the spectrum becomes extremely dense and complex; we did not attempt to carry the study into this region. Typical segments of the spectrum are shown in Fig. 1; these were typically made by averaging two to four scans over an interval of 10.23 nm, enough to cover about four bands. The entire

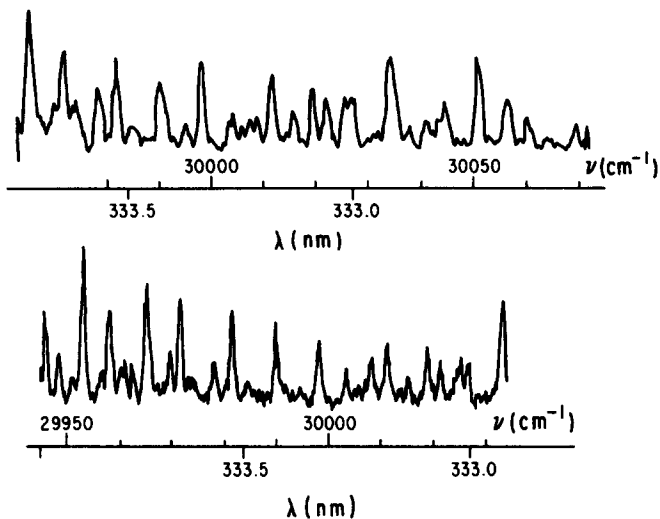


FIG. 1. Two typical traces of the fluorescence excitation spectrum of sodium iodide vapor in He.

excitation spectrum between 28 900 and 31 750 cm^{-1} (345 and 315 nm) is shown in Fig. 2(a). It consists of clusters of about 5 to 12 bands; and relatively weak lines outside the clusters, especially toward the red

end of the spectrum. The clusters are all similar and do seem to show progressions with intervals of about 40 to 75 cm^{-1} . However, the bands in the clusters have not yet been analyzed and will not concern us here, except insofar as they can be assigned to species other than monomeric NaI.

The excitation spectrum is too dense and too complex to be due simply to a ${}^1\Sigma^+ - {}^1\Sigma^+$ or $0^+ - {}^1\Sigma^+$ transition of a diatomic molecule. To gain any starting point for the analysis, it was necessary first to find one band that could be assigned with some confidence to the NaI molecule. This was achieved by finding a band in the excitation spectrum—in fact the band at 333.06 nm (30 025 cm^{-1} in vacuum)—whose fluorescence showed one band $257 \pm 12 \text{ cm}^{-1}$ to the red of the resonant fluorescence, and another emission band $255 \pm 12 \text{ cm}^{-1}$ to the red of the first. The slits of the fluorescence monochromator were approximately 1 mm wide, corresponding to a resolution of 0.4 nm or 36 cm^{-1} in this region of the spectrum. These two intervals are the well established separation of the levels $v'' = 0, 1$ and 2 of the $X^1\Sigma^+$ ground electronic state of NaI. Then the peaks to both sides of this excitation peak were studied in dispersed fluorescence until two more were found that have the same intervals. This gave a tentative interval and

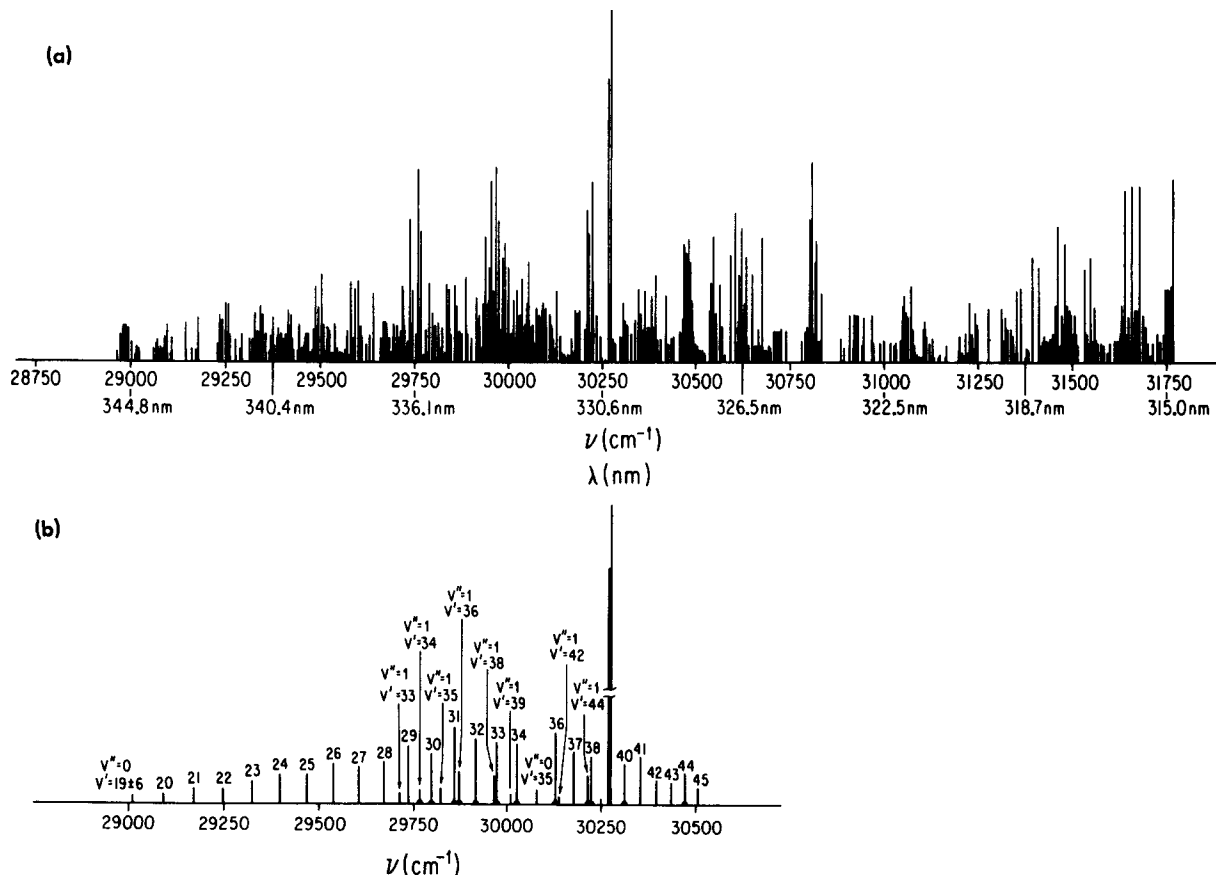


FIG. 2. (a) A schematic representation of the fluorescence excitation spectrum of sodium iodide vapor in helium, in the region 345–315 nm; (b) a schematic representation of the fluorescence excitation spectrum of the diatomic NaI molecule in the same region, extracted from (a) above; peaks with single numbers above them belong to the normal $v'' = 0$ progression and peaks belonging to hot bands have $v'' = 1$ written above the v' number. Peaks of (b) whose bases are solid half-circles are bands that have been observed in emission. The intense doublet at 30 266 cm^{-1} is due to the $4p - 3s$ transition of atomic sodium.

TABLE I. Fluorescence emission peaks.^a

$\lambda(\text{air})$	$\nu(\text{cm}^{-1}, \text{vacuum})$				
	v'	$v''=0$	1	2	3
$v' \leftarrow 0$					
335.51 nm	30	29 796	29 532	29 272	
334.84	31	29 856	29 594	29 348	
334.19	32	29 914	29 654	29 394	
333.56	33	29 970	29 711	29 459	
332.96	34	30 024	29 766	29 520	
331.82	36	30 127	29 864	29 613	29 360, 4
330.78	38	30 222	29 961	29 709	
329.82	40	30 310	30 054	29 789	
328.10	44	30 469	30 218	29 955	
$v' \leftarrow 1$					
335.84	34	30 022	29 767.4	29 512.9	
330.91	44	30 477	30 210.6	29 960	

^aAll frequencies are $\pm 12 \text{ cm}^{-1}$.

trend for the vibrational levels of the upper state. This interval could not be assumed to be close to ω'_e or ω'_0 because the avoided crossing picture suggests that the Franck-Condon-favored levels of the upper state are likely to be rather high above the minimum of the excited state. A number of levels were found that give emission peaks separated by the $v''=0-1$, $v''=1-2$ and in a few cases, the $v''=2-3$ intervals. Table I gives the fluorescence emission bands assigned to monomeric NaI by this method.

The next step in confirming the spectrum was the identification of hot bands in the excitation spectrum. These were found 257 cm^{-1} to the red of several bands already assigned tentatively to NaI in $v''=0$, and were confirmed by the presence of the characteristic "anti-Stokes" peak in fluorescence lying 257 cm^{-1} to the blue of the excitation peak. Then the v' progression built on $v''=1$ could be picked out. This progression is considerably shorter than that for the progression on $v''=0$, due presumably to the low population of $v''=1$. Despite careful searching, we could find no evidence for any absorption from levels with $v'' \geq 2$.

A further confirmation was necessary to establish the v' progressions. For several intervals between lines assigned tentatively to the v' progression on $v''=0$, excitation peaks between the suspected NaI peaks were examined in dispersed fluorescence. We found no excitation peak whose emission corresponds to that of the monomeric NaI molecule. Hence, we concluded that we had found two v' progressions of NaI, and that no others were present in the excitation spectrum in the interval we studied and under the conditions of our sample. Figure 2(b) shows these progressions schematically on the same scale as the full spectrum in Fig. 2(a). Table II gives the entire set of excitation bands and their assignments; note that the v' numbering is highly uncertain because the region of the excited state potential near its minimum is not observed. Bands listed in Table II but not in Table I were not studied in dispersed fluorescence. The assignments of these bands were made by extrapolating the vibrational frequency intervals obtained from

the bands listed in Table I.

The excitation bands assigned to unspecified molecules other than monomeric NaI were of two sorts. One kind has intervals in its emission spectrum like that of NaI but is shifted in its entirety from the excitation line by some 8 to 25 cm^{-1} to long wavelengths. This shift would suggest that such peaks were due to van der Waals molecules of carrier gas with NaI; however, we were unable to introduce significant changes in the shifts by changing carrier gas from He to Ar. They may be due to dissociation of weakly bound dimers or polymers of NaI itself. The other sort of emission spectrum appeared to be too complex to be due to monomeric NaI, and is tentatively attributed to some mixture of dimeric $(\text{NaI})_2$ molecules and higher polymers.

The observed spectrum was used to fit an upper-state potential curve. One form of this curve assumed to be exponential for $R < 3.25 \text{ \AA}$, and was spliced to a Morse potential at this distance. The Morse potential was fit through a spline to a Coulomb potential at $R < \sim 10 \text{ \AA}$, but this was outside the region accessible to us, so this long-range part of the fit is quite arbitrary. A second form was a steeper exponential joining a Morse curve at 3.35 \AA . A third form of potential was taken to be exponential out to $R = 3.88 \text{ \AA}$, then harmonic to the point symmetric to the first joining point and then Morselike. All these curves fit the intensities and frequencies of the observed bands assigned to NaI, to within the experimental uncertainties. The curves of the first and third potentials are shown in Fig. 3. Note that they are essentially identical in the energy range reached by vertical transitions from the ground state and along the left-hand branch down to about 1000 cm^{-1} above the atomic dissociation limit, but are quite different for $3.2 < R < 5.5 \text{ \AA}$. The first curve has an ω_e of 123.5 cm^{-1} and r_e of approximately 3.5 \AA ; the other shown has ω_e of 83.3 cm^{-1} and r_e of approximately 3.85 \AA . The uncertainty in the low portion of the curve naturally leads to a large uncertainty in the v' numbering, as Tables I and II indicate.

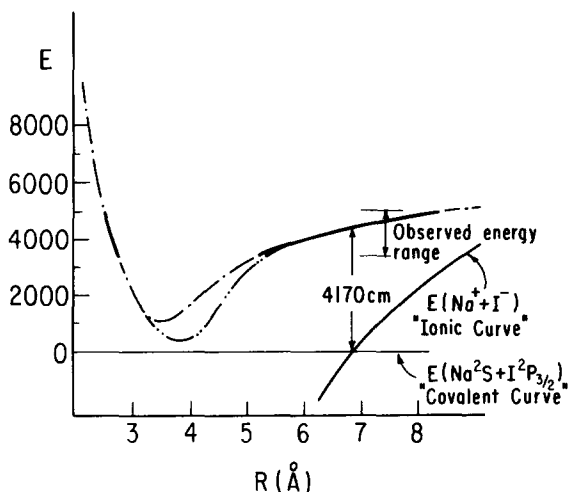


FIG. 3. Approximate potential curves for the observed bound excited state of the NaI molecule.

TABLE II. Fluorescence excitation peaks of NaI.

Frequency	Spacing	Relative intensity	Vibrational assignment $v'(\pm 6)$	Comments	
$v'' = 0$ Progression					
28 930 cm^{-1}	81 cm^{-1}	0.4 ± 0.3	18	the assignment of these bands is uncertain due to overlaps with other bands	
29 012	80	0.4 ± 0.3	19		
29 092	79	0.5 ± 0.3	20		
29 171	77	0.7 ± 0.3	21		
29 248	75	1.0 ± 0.4	22		
29 323	73	1.3 ± 0.3	23		
29 396	71	1.7 ± 0.3	24		overlap
29 468	69	2.0 ± 0.4	25		overlap
29 537	67	2.5 ± 0.4	26		
29 604	65	2.3 ± 0.5	27		
29 670	63	2.6 ± 0.5	28	overlap	
29 734	61	2.4 ± 0.3	29	overlap with hot band of non-NaI species	
29 796	60	2.5 ± 0.3	30	some overlap	
29 856	58	2.8 ± 0.3	31		
29 914	56	2.5 ± 0.3	32		
29 970	54	2.4 ± 0.3	33		
30 024	52	2.4 ± 0.3	34		
30 076	50	0.7 ± 0.3	35	very weak relative to other NaI bands	
30 127	48	3.1 ± 0.4	36	definite overlap with non-NaI band	
30 175	46	2.0 ± 0.4	37	overlap with intense complex band	
30 228	44	2.0 ± 0.4	38	overlap with Na doublet ($3s-4p$)	
30 266	42	1.6 ± 0.4	39		
30 310	41	1.6 ± 0.4	40		
30 351	39	1.3 ± 0.4	41		
30 394	37	1.1 ± 0.4	42	overlap with strong band	
30 432	35	0.8 ± 0.3	43		
30 469	34	0.9 ± 0.4	44		
30 504	32	0.7 ± 0.3	45		
30 538	30	0.6 ± 0.3	46		
30 569	29	0.5 ± 0.3	47		
30 598	27	0.6 ± 0.3	48		
30 626		0.3 ± 0.3	49	overlap	
$v' = 1$					
29 767	~ 51	0.5	34		
29 818	~ 51	~ 0.3	35		
29 869	~ 47	0.6	36		
29 917	~ 48	~ 0.2	37		
29 964	44	0.8	38		
30 009	43	0.5	39		
30 053	41	...	40	masked by a non-NaI band	
30 094	42	0.4	41		
30 136	38	~ 0.5	42		
30 175	36	...	43	masked by NaI cold band	
30 212	33	0.5	44	some overlap with non-NaI band, probably a van der Waals complex	
30 281		0.3	46		

INTERPRETATION

The most plausible interpretation of the bound excited state responsible for the spectrum described here is the conventional one, that it is a 0^+ or $^1\Sigma^+$ state exhibiting an avoided crossing with the ground state. This must remain only a plausible interpretation until a rotational analysis is performed on the spectrum. If we accept it as a working hypothesis, then the curve of either of

the potentials of Fig. 3 lies 4170 cm^{-1} above the energy of the atomic dissociation limit at the crossing distance of 6.93 \AA . This corresponds to a splitting of the adiabatic potentials of the two noncrossing 0^+ states of $8240 \pm 30 \text{ cm}^{-1}$, about seven times larger than the 1190 cm^{-1} average of the estimates made by Grice and Herschbach,¹³ the value which was used successfully by Los and Delvigne¹⁴ to interpret their experiments on collisional ion pair formation. The other exponential-

Morse curve gives a slightly smaller splitting, 3890 cm^{-1} . It would be worthwhile to try to reinterpret the experiments of Los and Delvigne on the basis of our much larger splitting.

The vibrational separations of the upper levels that we observe run from 82 cm^{-1} for $v' = 18$ to $v' = 19$ down to 28 cm^{-1} for $v' = 48$ to $v' = 49$ (all v' numbers are ± 6). To follow this spectrum all the way to the minimum of the upper state, one would have to search for bands in the region of $21\,335\text{ cm}^{-1}$ (4687 \AA) if the correct curve were like that shown in Fig. 3 with a minimum at 3.5 \AA , or in the region of $17\,493\text{ cm}^{-1}$ (5716 \AA) for the curve of Fig. 3 whose minimum is at 3.85 \AA . No absorption has been reported for NaI vapor in this region, but this is not surprising; at 3.5 \AA , the energy of the ground state potential is 5509 cm^{-1} and at 3.85 \AA , it is 8596 cm^{-1} . These are far enough above the level $v'' = 0$ for vibrational levels at these energies to remain populated only at the 0.5% level or below at the typical temperatures of 800–1200 K used for taking furnace spectra. It may, however, be feasible to conduct infrared-optical double resonance experiments to excited multiquantum excitation of molecules in the ground electronic state to vibrational levels between 5000 and 9000 cm^{-1} above $v'' = 0$ and then to excite fluorescence from these excited molecules.

The results of this work can be used with the observations of angular distributions of photofragments from NaI to draw some suggestive inferences regarding curve crossing in this molecule. The studies at 266 nm ⁷ cannot be compared with ours; we did not carry our spectra to such a high energy. The observations^{8,9} made with light at 347.1 nm also cannot be compared directly with ours: this wavelength, corresponding to approximately $28\,802\text{ cm}^{-1}$, is slightly longer than that of any transition of NaI that we observed, and corresponds to a frequency between the frequencies of $28\,849$ and $28\,767\text{ cm}^{-1}$ at which we would expect transitions from $v'' = 0$. It is possible that the excitation at 347.1 nm is inducing the transition we would assign as $v' = 23 - v'' = 2$; we expect this transition at $28\,811\text{ cm}^{-1}$. The linewidth of the laser used by Anderson *et al.* was 22 cm^{-1} . It is also possible that the absorption at 347.1 nm is due in large part to an underlying continuum which we would of course not detect in our fluorescence experiments. The essential result of the photodissociation experiments by Anderson *et al.* is that the process at 347.1 nm involves only $20 \pm 12\%$ parallel transitions if the process is interpreted as involving a long-lived 0^+ state and if the 0^+ state is responsible for all the parallel character and the 1 state, for all the perpendicular character.

One other possibility must also be addressed for all the photodissociation experiments. In view of the many bands observed that are not assigned as monomeric NaI, the possibility must now be considered that some of the absorption in the photodissociation experiments on NaI vapor might be due to molecules other than NaI itself. Certainly our hypersonic nozzle method is much more conducive to formation of polymers and van der Waals molecules than are methods based on effusive sources. However, the evidence presented here suggests that it

would be useful to conduct further investigations into the identity of the absorbers in the photodissociation experiments; mass analysis of the vapors might, e.g., be sufficient to rule out polymers.

The study of photodissociation of NaI most relevant to our work is that of Van Veen *et al.*,^{10,11} who used radiation covering the range from 300 to 337 nm, i.e., from $29\,670$ to $33\,330\text{ cm}^{-1}$. By measuring flight times of photodissociation products and their angular distribution, they inferred that the perpendicular transition from $X^1\Sigma^+$ to a state of $\Omega = 1$ commenced at a threshold energy of approximately 3.2 eV ($25\,800\text{ cm}^{-1}$) above the ground state minimum and that the threshold for the appearance of the parallel transition to the excited state of $\Omega = 0^+$ is at an energy approximately 3.58 eV ($28\,880\text{ cm}^{-1}$) above the ground state. They interpret the photodissociation of the 0^+ excited state as involving a quasibound intermediate with a lifetime long compared with the rotational period or the inverse separation of the relevant rotational quantum states of the excited molecule.

These results are consistent with ours under any of three conditions. The first possibility is that the transitions we observe at frequencies below $25\,800\text{ cm}^{-1}$ are not intense enough to contribute measurably to the photodissociation as observed by Van Veen *et al.* The second possibility, which we consider the most interesting, is that the lifetime of the 0^+ state depends on the degree of excitation, and that levels below $25\,800\text{ cm}^{-1}$ have radiative lifetimes longer than their lifetimes toward dissociation. The third possibility is that the photodissociation 0^+ state is simply not the same as the excited state we observe in fluorescence. This last possibility must of course be entertained, but not lavishly; the only other 0^+ state in the relevant energy range is the $^3\Pi_0^+$, for which we see no strong reason for any binding that would bring its internal energy significantly below the dissociation limit of $\text{Na}(^2S) = \text{I}^*(^2P_{1/2})$, at $33\,248\text{ cm}^{-1}$, well above the region where we and Van Veen *et al.* see transitions we attribute to a 0^+ state. The first possibility is unlikely because the intensity of absorption of the low-energy bands is only about half of that of the bands that would be responsible for detectable photodissociation, and because the sample irradiated by Van Veen *et al.* probably contains many more vibrationally excited molecules; the temperature of their NaI vapor was about 900 K. These would contribute to the detectable photodissociation spectrum at frequencies below $29\,040\text{ cm}^{-1}$ if that were not an effective threshold energy for photodissociation, at least in the sense that above $29\,040\text{ cm}^{-1}$, the photodissociation rate competes with the radiative rate.

This brings us to the remaining possibility, that $29\,040\text{ cm}^{-1}$ is the energy above which the photodissociation rate is comparable with the fluorescence rate. The vibrational interval in this region is approximately 80 cm^{-1} , corresponding to a vibrational period of $2.4 \times 10^{12}\text{ s}^{-1}$. The probability of curve crossing in NaI was estimated by Van Veen *et al.*, from the coupling model of Faist and Levine,¹⁵ to be 5×10^{-6} , so, with one crossing on the outward phase per oscillation, we find

a photodissociation rate of $1.7 \times 10^7 \text{ s}^{-1}$, or a lifetime of 59 ns. This value is based on a crude Landau-Zener model with Grice and Herschbach's splitting, rather than ours. Moreover, this estimate makes no allowance for the dependence of the rate on the vibrational energy of the oscillator. (With a splitting of 8240 cm^{-1} instead of 1190 cm^{-1} , a Landau-Zener calculation gives a crossing probability many orders of magnitude too small to account for the occurrence of any photodissociation.) However, it is comparable to the lifetimes of $\sim 20 \text{ ns}$ we measured crudely for a few of the peaks in the excitation spectrum of NaI, namely the 34-0 transition at $30\,024 \text{ cm}^{-1}$, the 38-0 transition at $30\,222 \text{ cm}^{-1}$, and the 34-1 transition at $29\,767 \text{ cm}^{-1}$.

The potential curves of Fig. 3 place the energy $V^*(R)$ of the upper state $29\,820 \text{ cm}^{-1}$ above the $v''=0$ level of the ground state, at the crossing distances R_x . This is roughly in the middle of the region we observe and corresponds to an energy between the levels numbered $v'=30$ and $v'=31$ in Table I. According to these curves, levels $v' \leq 30$ have their classical outer turning points at distances smaller than R_x . Hence, we expect the onset of photodissociation at an energy close to but, because of tunneling and deviations from the simple crossing-point model, a little below $29\,820 \text{ cm}^{-1}$. The onset reported by Van Veen *et al.*, as we said, is at about 3.58 eV or $28\,880 \text{ cm}^{-1}$, 940 cm^{-1} below $V^*(R_x)$. This onset is perhaps a bit lower than we might expect from our curves, but the picture seems qualitatively and nearly quantitatively consistent. It is our present interpretation that the parallel contribution to the photodissociation spectrum of Van Veen *et al.* is due to the same transition as the one we observe in fluorescence, that both are due to a $0^+ \rightarrow {}^1\Sigma^+$ absorption, that the lifetime for fluorescence is about 10^{-7} s throughout the region we observe and that

the lifetime for photodissociation decreases sharply in the region of $28\,880 \text{ cm}^{-1}$ because the outer branch of the upper state potential reaches the crossing distance at about that energy.

ACKNOWLEDGMENT

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