

mentary bands and therefore belong to NaI and not to an unidentified species.

Taking the completely recorded spectrum by Ragone³ the extrapolation from our assigned region to an assignment of the spectral segment in Fig. 1 of Ragone *et al.*¹ is straightforward and without ambiguity, including the lines in between. The structure of Fig. 1 consists of overlapping fragmentary bands of NaI.

Therefore, we conclude the reported spectrum in the paper by Ragone *et al.*¹ originates totally of the monomeric NaI, only a few lines may belong to different species. Probably no rotational cooling was achieved in their experiment because transitions with rotational quantum numbers of about 60 are as strong as those with $J \approx 20$. Lower J values are assigned only in a few cases.

Table II of the paper by Ragone *et al.*¹ shows transition frequencies and the proposed vibrational assignment. Taking, e.g., the bands at 30 432 and 30 469 cm^{-1} of successive vibrational quantum numbers, $v' = 43$ and $v' = 44$, respectively, our reassignment deduces that these transitions are the $P(61)$ and $R(58)$ lines of a single vibrational band. Therefore the difference of the two transitions does not represent any vibrational energy.

Similarly all energy spacings given in Table II of Ref. 1 contain a large amount of rotational energy and therefore any conclusion about the vibrational energy and the potential function of the excited state, as it was proposed by Ragone *et al.*,¹ is impossible unless the rotational assignment is taken into account.

This new analysis also removes the discrepancy of the reported splitting of the adiabatic potentials of the two noncrossing states (ionic and covalent, compare Fig. 3 of Ragone *et al.*) to be 8340(30) cm^{-1} in contrast to the calculations of Grice/Herschbach⁴ who obtained 1190 cm^{-1} . Our interpretation of the observed spectrum establishing fragmentary bands immediately shows that the excited state of NaI is intermediate between the limiting cases of a completely avoided crossing and of a very weak interaction of the ionic and covalent state. This is in good agreement with the result of Ref. 4.

¹A. S. Ragone, D. H. Levy, and R. S. Berry, *J. Chem. Phys.* **77**, 3784 (1982).

²S. H. Schaefer, D. Bender, and E. Tiemann, *Chem. Phys. Lett.* **92**, 273 (1982).

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⁴R. Grice and D. R. Herschbach, *Mol. Phys.* **27**, 159 (1974).

Reply to "Comment on 'Fluorescence spectra of the NaI molecule' "

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In their comment¹ and in their recent paper² Schaefer *et al.* have applied a theoretical treatment of Child³ to analyze their static gas and our supersonic free jet fluorescence excitation spectra of NaI. In our paper⁴ we reported the observation of a large number of spectral lines in the region 29 000–32 000 cm^{-1} . We were only able to assign a small fraction of the observed lines to NaI and suggested that the remainder were due to higher polymers of the form $(\text{NaI})_n$. A major assumption in our analysis was that the supersonic jet spectrum would be dominated by low J transitions. Since we would be unable to resolve low J rotational splittings, it followed that the very large number of lines could not be due to rotational structure and must therefore be due to something else, e.g., polymers or van der Waals molecules or both.

The analysis of Schaefer *et al.* proceeds from the assumption that NaI is a case of intermediate coupling between states built on adiabatic and diabatic potentials. The model of Child³ applied to such a case predicts that most rotational levels will rapidly dissociate and therefore be undetectable in a fluorescence experiment.

Only those few rotational levels where there is a near degeneracy between the limiting adiabatic and diabatic states will live long enough to fluoresce. Since these near degeneracies are accidental, they will occur at random values of J , and this will lead to a fluorescence excitation spectrum containing lines from a few adjacent high J levels with no observable lines at higher or lower J values. Since rotational splittings increase with increasing J , they propose that much or all of the structure in our spectrum is due to high J rotational structure of monomeric NaI and not due to other species.

The main point made by Schaefer *et al.*, that much of the structure in our spectrum is due to high J rotational splittings, is very likely correct. The static gas spectrum analyzed in Ref. 2 was in a region somewhat to the blue of our supersonic jet spectrum, and only the region of the spectrum from 30 600 to 31 100 cm^{-1} was assigned there. In their comment, Schaefer *et al.* extend their analysis to 29 900 cm^{-1} , using the model of Child to assign the peaks of our excitation spectrum to the monomer. It may well be that such an analysis based on the method in Ref. 2 can account

for many of the lines in our jet spectrum. However, the emission spectra from several of the excitation lines appear to be too complex to be assigned to diatomic molecules.

There are two secondary points made by Schaefer *et al.* that require some discussion. First, they assume that since they can assign features in our spectrum to high J lines, that there was no rotational cooling in our supersonic jet experiments. This need not be the case even if their rotational assignment is correct. Although one tends to speak of a "rotational temperature" in a free jet expansion, it is well known^{5,6} that under most expansion conditions the rotational state distribution is non-Boltzmann. In general, the population in the lower rotational levels is distributed according to a Boltzmann distribution at a low temperature, but there is usually an excess population of higher J states which sometimes⁶ can be described by a second Boltzmann distribution at a much higher temperature. In an ordinary molecule where the fluorescence quantum yield is more or less independent of J , this distribution produces a fluorescence excitation spectrum that is dominated by low J transitions but contains weak high J lines as well. If Schaefer *et al.* are correct in assuming that NaI is a case of intermediate coupling, then the fluorescence quantum yield of the low J states would be vanishingly small, and the cold jet fluorescence excitation spectrum would consist of only those weak high J lines which had a higher quantum yield. In our spectrum we observed weak vibrational hot bands originating from $v''=1$ but were unable to observe transitions from higher vibrational levels of the ground state. This suggests that we were getting vibrational cooling, and it is highly unlikely that the molecules could be vibrationally cold while remaining rotationally hot. It seems far more likely that we were observing transitions from the sparsely populated fluorescing levels of a cold rotational distribution, the more highly populated levels being unobservable due to low quantum yield.

If this suggestion is correct, it means that sodium iodide is the one known example where supersonic jet spectroscopy provides no advantage and produces a severe disadvantage as compared to static gas spectroscopy. The usual advantages of supersonic jet spectroscopy are twofold. First, it depopulates a large number of rotational and vibrational levels thereby greatly simplifying the spectrum. Second, it concentrates the population in a few observable levels increasing the signal strength. If Schaefer *et al.* are correct, the static gas fluorescence excitation spectrum is already

simplified by the predissociation of most of the rotational levels, and all that supersonic cooling accomplishes is to remove population from the observable levels.

A second point that needs discussion is the comparison of those few lines that we have assigned to monomeric NaI with the assignment and analysis of Schaefer *et al.*² In their paper² they state that we derive a value of $\omega'_e = 118.4 \text{ cm}^{-1}$ for the vibrational constant of the excited state, and that this is in strong disagreement with the values of $\omega(\text{diabatic}) = 32.8 \text{ cm}^{-1}$ and $\omega(\text{adiabatic}) = 39.4 \text{ cm}^{-1}$ which they quote in their Table 3. In fact no such disagreement exists between the two sets of data, the apparent discrepancy arising from the fact that two different quantities are being compared. Both experiments involved transitions terminating in highly excited vibrational levels of the excited electronic state, the 0-0 band being unobservable due to a small Franck-Condon factor. Since the excited state is very anharmonic, the spacings between highly excited vibrational levels are very much smaller than ω'_e . The value of $\omega'_e = 118.4 \text{ cm}^{-1}$ attributed to us must refer to the harmonic constant extrapolated from the observed high v' levels, and in our paper we emphasize that the spacings of the v' levels change rapidly with v' , so that extrapolation to find ω'_e cannot be very reliable. The values $\omega = 32.8, 39.4 \text{ cm}^{-1}$ taken from the static gas spectrum² are measures of the vibrational spacings in this region. For example, we observe a splitting of 37 cm^{-1} between adjacent vibrational transitions at $30\,212$ and $30\,175 \text{ cm}^{-1}$ while Schaefer *et al.*² observe a splitting of 34 cm^{-1} between transitions at $30\,969$ and $30\,935 \text{ cm}^{-1}$. Whatever might be said of our unassigned lines, the vibrational structure of those lines that we did assign seems to agree quite well with that of Ref. 2.

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