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Electronic band-shape calculations in ammonia

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The vibronic nature of the lowest energy electronic absorption and of the lowest energy photoelectron spectrum of NH_3 are investigated theoretically. Two-dimensional Franck–Condon factor calculations are performed and theoretical spectra are constructed including the effect of vibronic linewidth. The comparison of the experimental with theoretical spectra, computed under various assumptions, leads to several conclusions. The conspicuous continuum underlying the $\tilde{A} \leftarrow \tilde{X}$ transition is seen to arise from the overlapping tails of vibronic line shapes. There is no need to attribute the continuum to a second electronic transition. The ν_1, N–H stretching mode, is excited in both the electronic absorption and photoelectron spectrum. The $\tilde{A}$ state of NH_3 may be able to support two quanta of ν_1. The planar NH_3^+ ion has a N–H bond longer than in the ground state NH_3 by about 0.06 Å.

I. INTRODUCTION

Ammonia in its electronic ground state is usually taken to have the pyramidal (C_{3v}) geometry with a $(1a_1)^2(2a_1)^2(1e)^4(3a_1)^2$ orbital configuration. The lowest excited singlet state is planar (D_{3h}) at equilibrium and is formed by promoting an electron from the lone pair $n(3a_1$ in C_{3v} or $1a_2''$ in $D_{3h})$ orbital to a Rydberg $3sa_1'$ orbital, resulting in an electronic state with A_2'' symmetry.[1] The $\tilde{A}(A_2'') \leftarrow \tilde{X}(^1A_1')(D_{3h})$ transition is allowed and is characterized by a long progression in the out-of-plane bending ν_2 mode, resting on top of an apparent continuum absorption.[1] No discrete rotational structure can be observed due to a fast predissociation process giving $NH_2(^2B_1)+H(^2S)$.[1] Two different interpretations of this predissociative process have been given. In one, a "near intersection" was proposed between the $\tilde{A}(^1A_2'')$ Rydberg state with a second, repulsive $^1A_2''$ state.[2] To account for such a second low lying $^1A_2''$ state, the continuum underlying the $\tilde{A} \leftarrow \tilde{X}$ transition was associated with the conjugate intravalence transition $4a_1' \leftarrow 3a_1(1a_2'')$.[3] In a second interpretation, the potential barrier to dissociation arises because as the N–H bond distance increases the $3s$ orbital evolves into a σ^* N–H orbital, and finally to a hydrogenic $1s$ orbital.[4] The nature of the vibrational structure in the $\tilde{A} \leftarrow \tilde{X}$ spectrum also has been the subject of debate. While the extended progression of ν_2 appears to fully characterize the absorption spectrum, attempts to explain this structure in terms of calculated Franck–Condon (FC) factors for a ν_2 progression alone have not been very successful.[5] Two different approaches were put forth to overcome the apparent failure of a simple one dimensional FC treatment. In one,[6] it was suggested that the electronic transition moment decreases as the molecule is flattened. In another[7] it was recognized that a progression in the totally symmetric, N–H stretching, ν_1 mode should also be excited, since it is known that the equilibrium N–H bond is changed upon excitation to the $\tilde{A}$ state.[1] In order for a ν_1 progression not to be exposed as additional structure (not seen in the spectrum) the upper state ν_1 frequency was taken to be about three times the excited ν_2 frequency.[7,8]

The photoelectron spectrum of NH_3 has been obtained by several groups of investigators.[9–12] The lowest ionization potential involves the ionization of the lone pair; i.e., it represents the transition $(\ldots 1e^4 3a_1^1)\,^2A_1(NH_3^+) \leftarrow (\ldots 1e^4 3a_1^2)\,^1A_1(NH_3)(C_{3v})$ leading to a planar ground state of the ion. Here, too, the band structure appears to be characterized by a simple extended progression in the ν_2 vibration. In early low resolution experiments,[10] the progression reaches a maximum at $v=5$. However, arguments fully analogous to those related to the $\tilde{A} \leftarrow \tilde{X}$ transition of NH_3 led to the expectation that the photoionization spectrum should exhibit a progression of the ν_1 mode as well. And a subsequent high resolution photoelectron spectrum[12] revealed evidence for ν_1 excitation. Rosenstock and Botter[8,13] and Harshbarger[14] investigated theoretically the FC activity of ν_1 in the photoelectron spectrum. Botter and Rosenstock[13] found that the FC activity of the ν_1 mode could be quenched provided that the N–H bond length decreases by about 0.06–0.07 Å upon ionization. Alternatively, however, they found[8] that the best agreement with the FC structure reported by Branton *et al.*[10] was encountered when there was no change in the N–H bond length, or a slight compression of it in the excited state. Under these conditions, FC promotion of the stretching frequency must occur, so that ν_1, ν_2 combination bands are responsible for some of the band intensity at higher energies. On the other hand, Harshbarger[14] found good agreement with observation[10] if the N–H bond length is taken to increase by 0.06 Å upon ionization. Again, combination bands are present. In either case the lack of any structure assignable to ν_1 promotion had to be rationalized by taking $\nu_1 \simeq 3\nu_2$.

At the top in Fig. 1, the $\tilde{A} \leftarrow \tilde{X}$ NH_3 absorption spectrum obtained by Tannenbaum *et al.*[15] is reproduced. The lower part of Fig. 1 is the photoelectron spectrum obtained by Rabalais *et al.*[12]

The present work constitutes a new theoretical study of these two electronic transitions in ammonia, the $\tilde{A} \leftarrow \tilde{X}$ transition and the lowest energy transition in the photoelectric spectrum. In the C_{3v} ground state, the ν_1 stretching and ν_2 bending coordinates are mixed,

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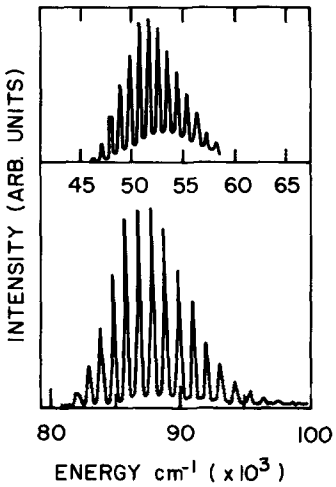

FIG. 1. Top: The $\tilde{A} \leftarrow \tilde{X}$ electronic absorption spectrum of NH_3 adapted from Ref. 15. Bottom: The first photoelectron band of NH_3 adapted from Ref. 12.

giving normal modes. In the D_{3h} upper states they are of different symmetry, and there is no mixing. These two pure symmetry valence coordinates are themselves the proper normal coordinates. FC calculations in such a case do not separate into one-dimensional problems. Full two-dimensional integrations have been carried out using a uniquely determined force field for the ground state of ammonia. Furthermore, FC spectra are constructed which incorporate the observed widths of the vibronic transitions. On the basis of the calculated spectra, conclusions are made regarding the nature of the continuum of the $\tilde{A} \leftarrow \tilde{X}$ transition, the FC activity of the ν_1 mode upon excitation/ionization, the relative widths of the ν_1 and ν_2 bands, the N–H bond length in NH_3^+, and the binding along the N–H coordinate in the $\tilde{A}$ NH_3 and $\tilde{X}$ NH_3^+ electronic states.

II. COMPUTATIONAL PROCEDURE

The band shape of an electronic transition within the Born–Oppenheimer approximation, and with neglect of the dependence of the electronic transition moment on nuclear coordinates, may be approximated by

$$W(\nu, T) = \frac{1}{2\pi} \sum_i B_i(T) \sum_N \frac{\Gamma_{iv} |\langle v|i\rangle|^2}{(E_{vi} - h\nu)^2 + (\Gamma_{iv}/2)^2} , \quad (1)$$

where $|\langle v|i\rangle|^2$ is the FC factor which couples vibrational level $|i\rangle$ of the ground electronic state with vibration level $|v\rangle$ of the excited electronic state, Γ_{iv} is the associated linewidth, E_{vi} the transition energy, and B_i is the normalized Boltzmann weighting factor for the ith level of the ground state. $W(\nu, T)$ is normalized to unity for integration over the full range of incident light frequency ν. Since formal rotational structure is not present in Eq. (1), this equation must be considered as only approximate, unless the homogeneous broadening of rotational lines greatly exceeds the separation of the rotational lines associated with the individual vibronic transitions. To the extent that this is not the case, the Lorentzian shape and Γ_{iv} cannot refer to simple homogeneous structure and must be taken, in part, as simply an effort to simulate a complicated vibronic line shape.

In applying Eq. (1) to the ammonia problem, the $3N$-6 dimensional nuclear coordinate space of $|i\rangle$ and $|v\rangle$ can be restricted to only two dimensions consisting of the totally symmetric N–H stretching motion (ν_1 mode) and the N–H bending or inversion motion (ν_2 mode). Thus, $|v\rangle = |v_1 v_2\rangle$ and $|i\rangle = |i_1 i_2\rangle$. It is these motions which may exhibit FC activity within the constraints of a C_{3v} point group. Furthermore, with a ν_1 frequency of 3 506 cm^{-1} and a ν_2 frequency of 1 021 cm^{-1} in the ground state,[16] we can take $B_i = B_{i_1, i_2} = 0$ for $i_1, i_2 \neq 0$ and thus $B_{0,0} = 1$ at room temperature. However, both the + and − tunneling components of the ground vibrational level which are split by only 0.97 cm^{-1} are about equally populated, and therefore transitions to both + and − upper states are allowed. Finally, the linewidth $\Gamma_{vi} = \Gamma_{v_1, v_2; 0,0}$ will be written simply as Γ_{v_1}. This introduces the simplification that the linewidth will not vary with the quantum number of the bending mode, but may do so with that of the stretching mode. This simplification will be discussed below. Thus for calculating band shapes of electronic transitions in ammonia when discrete rotational structure is absent, a simplified starting point is

$$W(\nu) = \sum_{v_1} W_{v_1}(\nu) , \quad (2a)$$

with

$$W_{v_1} = \frac{\Gamma_{v1}}{2\pi} \sum_{v_2} \frac{|\langle v_1 v_2 | 0, 0\rangle|^2}{(E_{v_1 v_2; 0,0} - h\nu)^2 + (\Gamma v_1/2)^2} . \quad (2b)$$

The calculation of the band profile proceeds then as follows. All two-dimensional FC factors $|\langle v_1, v_2 | 0, 0\rangle|^2$ are calculated using the harmonic oscillator approximation in the Sharp and Rosenstock[17] formalism. This theory can handle cases where there is a geometry change between the combining electronic states and the FC problem cannot be factored completely into one-dimensional FC integrals. To apply the Sharp and Rosenstock formalism,[17] a Wilson[18] G–F normal mode analysis is needed for each of the two electronic states. As noted, in a planar (D_{3h}) state the pure stretching and bending motions are themselves normal modes. These are properly normalized, given the elements of the G matrix. Thus, for the FC problem, one requires the force field of only the ground electronic state, the equilibrium geometry of each combining state, and the normal frequencies in the excited electronic state. The frequency of the N–H stretching motion in the A state is unknown since there is no sign of its presence in the absorption profile. Yet calculations reveal that the stretching mode ought to show considerable FC activity. As previously noted, this activity may be disguised by a near coincidence of one quantum of the stretching mode with three quanta of the bending mode. In the present work, an exact coincidence is assumed, i.e., $\nu_1 = 3\nu_2$ in the excited state, but the significance of such a coincidence may be blurred, depending on the magnitude of the linewidth factor Γ_{v_1}. This point will be discussed in more detail in the next section. The parameters used by us for the Sharp and Rosenstock[17] type FC calculations are collected in Table I. Unlike in previous work, the force field used in the present calculations is the quadratic force field of Duncan and Mills.[20] The symmetry

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TABLE I. The parameters.

	$\tilde{X}(^1A_1)$	$\tilde{A}(^1A_2'')$	Ion $\tilde{X}(^2A_1)$
ν_1 (cm^{-1})	3506[a]	2634	2740[e]
ν_2 (cm^{-1})	1021[a]	878	950[e]
r_e(N–H) (Å)	1.012[b]	1.08[d]	
β_e (deg)	67.9[b]	120[d]	120[e]
F_{11}, F_{12}, F_{22}	7.075, 0.851, 0.634[c] (mdyn/Å)		

[a]Reference 16.
[b]Reference 19.
[c]Reference 20.
[d]Reference 1.
[e]Reference 12.

coordinate basis used here is $S_1 = (1/\sqrt{3})\sum_{j=1}^{3}\Delta r_j$ and $S_2 = (r_e/\sqrt{3})\sum_{j=1}^{3}\Delta\beta_j$, where Δr_j is the stretching displacement of the jth N–H bond and $\Delta\beta_j$ is the change in the angle subtended by the jth pair of adjacent N–H bonds due to the bending motion. The force constant matrix elements F_{11}, F_{12}, and F_{22} cannot be uniquely determined, knowing only the ground state ν_1 and ν_2 frequencies. Duncan and Mills[20] have shown that a unique F matrix is best obtained by fitting the field to experimental vibration–rotation interaction constants and centrifugal stretching constants. They found that the NH_3 ground state has a *positive* S_1–S_2 interaction constant F_{12}. However, the force field utilized by Harshbarger[14] in the harmonic FC calculations of NH_3^+ and apparently also[7] in the NH_3 calculations has a *negative* interaction constant.[14] The sign (as well as the magnitude) of the interaction constant is quite influential in the FC calculations. Once the two-dimensional FC factors have been calculated, the sum in Eq. (2b) is performed for a discrete set of frequencies ν to obtain the band profile to be associated with a given value of the stretching quantum number v_1 (and Γ_{v_1}) in the excited electronic state. These separate, overtone-based, bending progressions, each with a chosen Γ_{v_1}, are then superimposed [Eq. (2a)]. The program developed by Korenowski[21] for performing these sums was adapted to this problem.

III. RESULTS AND DISCUSSION

A. The $\tilde{A}(^1A_2'') \leftarrow \tilde{X}(^1A_1'')$ transition of NH_3

Figure 2(a) shows the calculated $\tilde{A} \leftarrow \tilde{X}$ FC spectrum generated by assuming that only the bending ν_2 mode is excited in the upper state, i.e., $v_1 = 0$, $\Gamma_0 = 320$ cm^{-1}). The experimental intensities are also indicated by an asterisk for comparison. While the calculated spectrum is correctly peaked at $v = 6$, the peak by peak agreement with the experimental curve is not good. However, already one important conclusion can be made from this calculated spectrum. A continuum underlying the structured band evidently can be formed simply from the overlap of the broadened vibronic lines. The calculated continuum of Fig. 2(a), however, is symmetric, not skewed, as the one observed experimentally (Fig. 1, top).

In Fig. 2(b), we show the calculated spectrum generated when both the ν_2 and ν_1 modes are excited in the $\tilde{A}$ state and have the same linewidth; $\Gamma_{v_1} = \Gamma_0 = 310$ cm^{-1} for all v_1. The peak by peak agreement remains unsatisfactory and, in addition, the continuum does not have the observed skewed shape. Next the linewidths are decoupled. We permit the linewidth when the stretching mode is excited to exceed that when it is unexcited. Thus $\Gamma_{v_1} > \Gamma_0$ (for $v_1 > 0$). Agreement with experiment is best when $\Gamma_{v_1} \simeq 2.5\Gamma_0 (v_1 \geq 1)$, with $\Gamma_0 = 230$ cm^{-1}. The spectrum calculated under these conditions is shown in Fig. 2(c). The vibronic intensities, especially of the higher energy peaks, agree very well with experiment, although disagreement remains for the first few members of the bending progression. Furthermore, the overall intensity and the skewed shape of the continuum now is rather well duplicated. That $\Gamma_{v_1} > \Gamma_0$ for $v_1 > 0$ is reasonable follows if we recall that the predissociation of the $\tilde{A}$ state; i.e., $NH_3 \rightarrow NH_2 + H$ takes place along the N–H coordinate. The ν_1(N–H stretch) in the

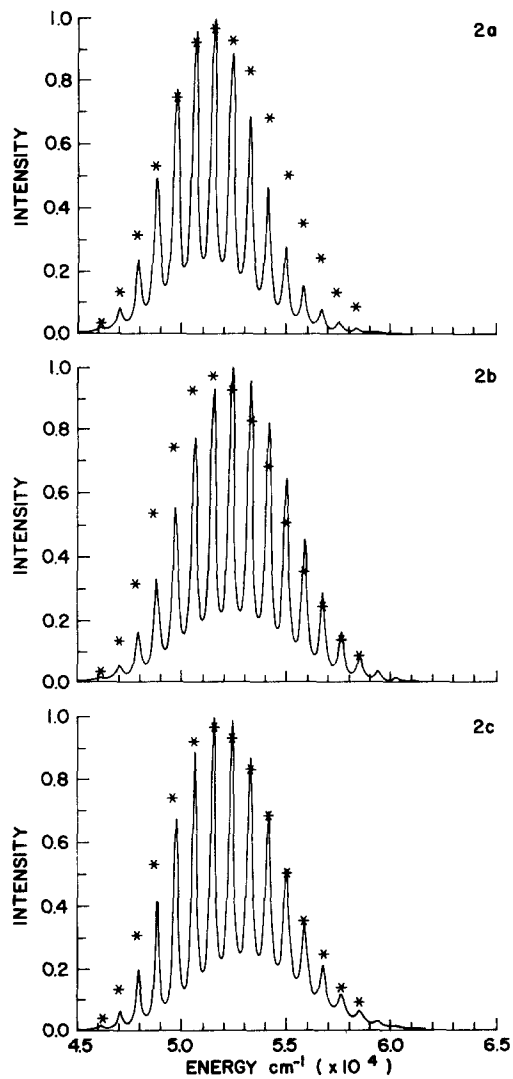

FIG. 2. Comparison of experimental and theoretical $\tilde{A} \leftarrow \tilde{X}$ absorption spectra. The experimental intensities from Ref. 7 are indicated by an asterisk. The theoretical spectra presented have been computed under the following conditions: (a) Only the out-of-plane bending ν_2 mode is excited in the $\tilde{A}$ state and $\Gamma_0 = 320$ cm^{-1}; (b) both the N–H stretch ν_1 mode and the ν_2 mode are excited in the $\tilde{A}$ state. The excited state frequencies satisfy the conditions $\nu_1 = 3\nu_2$ and the widths $\Gamma_{v_1} = \Gamma_0 = 310$ cm^{-1} for all v_1; (c) as in (b) but with $\Gamma_0 = 230$ cm^{-1} and $\Gamma_{v_1} = 2.5\Gamma_0$ ($v_1 \geq 1$).

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excited state is, therefore, the dissociative mode and as this mode is excited, a hastening of the predissociation is not unexpected. The ν_2 bending mode, however, is not a dissociative mode and does not couple to the ν_1 mode in zeroth order, since ν_1 and ν_2 belong to symmetry species a_1' and e', respectively, in the $\tilde{A}$ state.

The successful calculation of an underlying continuum as shown in Fig. 2(c) shows that the observed continuum is derived from the finite linewidth of the vibronic lines. It is not necessary to propose the presence of a separate repulsive state, e.g., an $\sigma^* \leftarrow n$ state, as has been done in the past.[3] The fact that there is no low lying valence state, at least at the ground state geometry, is also supported by recent quantum chemical calculations.[4,22,23] The alternative interpretation[4] of a barrier in the predissociation, which involves the "valenation"[24] of the 3s orbital with increasing N–H bond length, appears more plausible. In computing the spectrum of Fig. 2(c), we have considered the excitation of one and two quanta of ν_1 in combination with the quanta of ν_2 (excitation of higher levels of ν_1 does not significantly affect the spectrum). When the second quantum of ν_1 is not included, the agreement with experiment is now worse. Evidently ν_1 FC intensity to the blue of the $v_1 = 1$ vibronic level is needed. The present calculations achieve this within the harmonic calculations by introducing the $v_1 = 2$ level. However, the possible onset of anharmonicity or even bound-continuum transitions in this energy region cannot be excluded. Thus, the good fit obtained here by including a second quantum of the ν_1 mode does not necessarily prove that the upper potential in this coordinate is able to support at least two quanta of this mode. The predissociation process most probably involves proton tunneling through the potential barrier even from the $v_1 = 0$ level. Generally speaking, the larger the v_1, the more readily is the barrier penetrated. Thus $\Gamma_2 > \Gamma_1 > \Gamma_0$, but the refinement that $\Gamma_2 > \Gamma_1$ was not attempted in these calculations.

It is still necessary to comment on our assumption that in the $\tilde{A}$ state we have taken $\nu_1' = 3\nu_2' = 2634$ cm^{-1} (the prime refers to the $\tilde{A}$ state). Harshbarger[7], who did not explore the effects of finite linewidths on the spectrum, proposed a ν_1' frequency 10% higher than $3\nu_2'$. This choice optimized the agreement between his FC calculations and experiment. To test how severe the requirement that $\nu_1' = 3\nu_2'$ seems to be, a spectrum was constructed, as before, using the FC intensities and frequencies ($\nu_1' = 3.3\nu_2'$) given by Harshbarger.[7] Even with $\Gamma_{\nu_1} = \Gamma_0$ as large as 250 cm^{-1} (so as to blur the structure) the spectrum, thus constructed, reveals additional structure not seen experimentally. Further increasing Γ_{ν_1} can cause this new structure to merge into one broad peak. However, this only increases the overall linewidths which, already at $v_2 = 3$, are more than twice those seen (because $\nu_1' \neq 3\nu_2'$), even before the explicit structure is thus blurred. It seems that the ν_1' frequency must be quite close to $3\nu_2'$ in the $\tilde{A}$ state. Finally, we comment on the interpretation of the structure in the $\tilde{A} \leftarrow \tilde{X}$ spectrum offered by Durmaz *et al.*,[6] namely, that the FC factor anomaly arises because the electronic transition moment becomes greater as the planar molecule is bent, and no excitation of the ν_1 mode in the $\tilde{A}$ is considered. First, we note that excitation of the ν_1 mode is unavoidable because of the increased N–D bond length obtained by analyzing the rotational structure of the $\tilde{A} \leftarrow \tilde{X}$ transition in ND_3.[1] Furthermore, vibronic transitions involving ν_1 excitation in the ground state are observed in the $\tilde{A} \rightarrow \tilde{X}$ fluorescence spectrum of ND_3.[25] But more directly, electron impact studies at various scattering angles[7] give no indication of any significant variation of the transition dipole moment across the absorption spectrum.[25]

B. The $^2A_1(NH_3^+) \leftarrow {}^1A_1(NH_3)$ photoelectron spectrum

The calculations of the structure of the photoelectron spectrum rest on the results of the most recent, higher resolution experiments of Rabalais *et al.*[12] (Table I). The procedure is the same as outlined for the $\tilde{A} \leftarrow \tilde{X}$ transition in NH_3. Now, however, the N–H distance in the $^2A_1'$ state of the ion is not known. The two-dimensional FC calculations were therefore performed as a function of the N–H bond length of a planar NH_3^+. The same ground state parameters for NH_3 as before were used. The best agreement with experiment was found when the N–H bond length in NH_3^+ exceeded by 0.06 Å that in NH_3($\Gamma_{\nu_1} = \Gamma_0 = 230$ cm^{-1}). The spectrum is shown in Fig. 3. Under these conditions, the peak-to-peak calculated intensities agree with the experimental ones to within 10% or better. The continuum is also found to be significantly reduced in accord with the most recent photoionization studies.[12]

As mentioned above, Rosenstock and Botter,[8,13] found that compression of the N–H bond by 0.06 Å eliminates FC activity of the stretching frequency in the NH_3^+ spectrum (and removes the requirement that $\nu_1 = 3\nu_2$). For this case, ν_1 of NH_3^+ was taken equal to that in the neutral NH_3. The observed FC structure, however, is not well reproduced. We find that a compression of the N–H bond by 0.06 Å on ionizing NH_3 gives very poor agreement with observation. In the present work, ν_1 in the ion is taken to be 2740 cm^{-1}.[12] Furthermore, contrary to the findings of Rosenstock

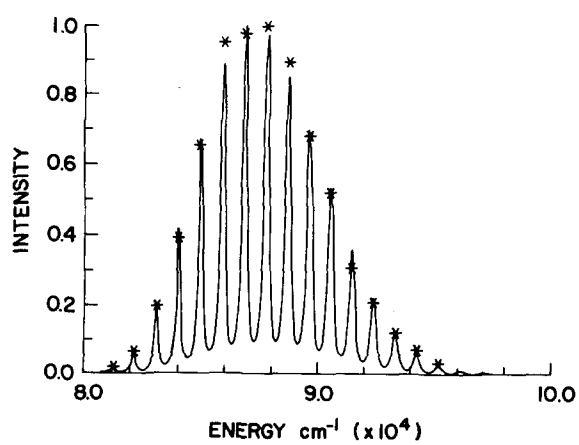

FIG. 3. Theoretical $^2A_1(NH_3^+) \leftarrow {}^1A_1(NH_3)$ photoelectron spectrum calculated under the following conditions: Both the ν_1 and ν_2 modes are excited, $\nu_1(NH_3^+) = 2740$ cm^{-1}, $\nu_2(NH_3^+) = 950$ cm^{-1}, and $\Gamma_0 = \Gamma_{\nu_1} = 230$ cm^{-1}. The N–H bond length in the ion was taken to be longer than that in the neutral by 0.06 Å.

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and Botter,[8] we find that agreement is also not good when there is no change (or a slight compression) in the N–H bond length. The force field used in the FC calculation by Rosenstock and Botter[8,13] was not specified. We suspect that differences between their work and ours can be attributed principally to the use of different force fields. In addition, we have chosen the more recent, higher resolution spectrum[12] for comparing calculations with experiment. That the N–H bond is longer in the ion than in NH_3 is supported now by *ab initio* quantum chemical calculations.[26] Interestingly, Harshbarger reached the conclusion that the N–H bond length in NH_3^+ is 1.07 Å, just as we have. However, he (as apparently did Rosenstock and Botter) fitted the earlier low resolution photoelectron spectrum of Branton *et al.*[10] and used a harmonic force field for the ammonia ground state having an interaction constant opposite in sign to the Duncan and Mills field[20] used here. The agreement between the two calculations must be coincidental. As in the case of the $\tilde{A}$ state of NH_3, we find that at least two quanta of ν_1 need to be excited in order to obtain good agreement with experiment. This suggests a stable NH_3^+ and is in agreement with the studies of Wight *et al.*,[27] which show no other photofragment besides NH_3^+ when NH_3 is ionized with photon energies <15 eV. The stability of NH_3^+ justifies using $\Gamma_{v_1} = \Gamma_0$.

IV. CONCLUSIONS

The two-dimensional FC calculations using the Duncan and Mills[20] force field for the $\tilde{X}$ state of NH_3 show that the ν_1 (N–H stretch) mode must be excited in both the $\tilde{A} \leftarrow \tilde{X}$ absorption spectrum and the $^2A_1 \leftarrow {}^1A_1$ photoelectron transition, although no spectral structure betrays its presence. The $\tilde{A}$ state frequency of ν_1 is estimated to be ~2630 cm^{-1} (i.e., about three times the ν_2 frequency in the $\tilde{A}$ state).

The underlying continuum follows simply from the overlap of vibronic transitions having finite widths. In the $\tilde{A} \leftarrow \tilde{X}$, the continuum is skewed to higher energy. This is rationalized by proposing that the $v_1 = 1$ and $v_1 = 2$ levels are shorter lived than the $v_1 = 0$ level ($\Gamma_{v_1} = 2.5\Gamma_0$). Thus, the conspicuous continuum of the $\tilde{A} \leftarrow \tilde{X}$ electronic transition does not require the presence of a second underlying transition.

The present calculations imply that the potential surfaces of $\tilde{A}(NH_3)$ and $\tilde{X}(NH_3^+)$ along the N–H coordinate can support at least two quanta of the N–H stretching mode. NH_3^+ is apparently regarded as a stable ion.[27] However, the $\tilde{A}$ state of NH_3 is highly predissociative, and effects due to anharmonicity in the ν_1 mode and even bound-continuum transitions may be an alternate to requiring FC activity of two harmonic quanta of ν_1. The planar ground state of NH_3^+ has an N–H bond *longer* than that of the neutral by about 0.06 Å.

ACKNOWLEDGMENT

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