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Resonant vibrational excitation of methylamine by low energy electron impact

F. Motte-Tollet,[a] M.-J. Hubin-Franskin,[b] and J. E. Collin
Laboratoire de Spectroscopie d'Electrons diffusés Université de Liège, Institut de Chimie- Bât. B6, Sart Tilman par 4000 Liège 1, Belgium.

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The study of the excitation functions of the NH_2 and CH_3 stretching modes of methylamine in the 4–12 eV electron impact energy range shows evidence of a broad shape resonance built on the electronic ground state and centered at 7.5 eV. This resonance is formed by the trapping of the incident electron in the second unoccupied molecular orbital and is of A'' symmetry. The elastic and inelastic angular differential cross sections measured in the 10°–90° range suggest a dominant *p* character. A second shape resonance located at higher energy contributes mainly to the enhancement of the CH_3 deformation modes and is very likely of A' symmetry. A comparison is made between the resonances observed in NH_3 and CH_3NH_2. The effect of the methyl substitution is briefly discussed.

I. INTRODUCTION

This work is related to a small polyatomic molecule CH_3NH_2 for which the spectroscopy of the lowest energy molecular orbitals has been studied by electron impact.[1-4] The literature suggests that the energies of the electronic states of methylamine are similar to that of the ammonia molecule, the energies being only a bit lower.[5,6] Another way to get information about the spectroscopy and the spatial charge distribution of the unoccupied molecular orbitals is the study of the resonances of negative ions by low energy electron impact.

In NH_3, two negative ion resonances are known to occur in the 5–10 eV electron impact energy range. First, a Feshbach type one is centered at 5.7 eV and decays at least partly by dissociative attachment.[2,7-10] Second, a shape resonance centered at 7.3 eV enhances the NH_2 stretching vibrational modes $\nu_{1,3}$ of the electronic ground state of the molecule. The latter is formed by the temporary trapping of the incident electron behind a barrier in the electron–molecule interaction potential in the second unoccupied molecular orbital 2*e*, so that the negative ion electronic state is ^2E.[11]

For methylamine, fragment negative ions have been reported in dissociative attachment studies.[7,12] The maxima in the cross sections have been observed for H^- at 5.5, 6.8, and 9.5 eV, for NH_2^- at 6.4, 9.9, and 11.8 eV, for NH^- at 10.5 eV, for CN^- at 2.52 and 8.34 eV and for CNH_4^- at 5.5 eV. The SF_6^-/CH_3NH_2 threshold excitation spectrum is dominated by a band at 5.4 eV,[13] which may be due to the excitation of the lowest triplet state[2,4] populated directly and/or indirectly through a resonance by emission of zero energy electrons.

We have investigated the vibrational excitation of gaseous methylamine by the electron energy loss method for impact energies ranging from 4 to 12 eV. Until now, vibrational excitation by electron impact has been reported only for methylamine adsorbed on various metallic substrates.[14]

We have recorded the electron energy loss spectra at 30 eV and 7.2 eV for various scattering angles. Relative excitation functions of the various vibrational modes of the electronic ground state corresponding to $\Delta v = 1$ transitions have been measured in the 4–12 eV energy range. Finally, we also have reported the relative elastic and vibrational differential cross sections as a function of the scattering angle (10°–90°) at 7.2 eV.

II. EXPERIMENT

The apparatus used for the present measurements is a Vacuum Generator SEELS 400, modified for work on gaseous target. It has been described in detail elsewhere.[5] Briefly, it consists of an electron gun, a 150° hemispherical-sector electrostatic electron monochromator, a collision region and an analyzer of the same type as the monochromator rotatable from $-35°$ to $+120°$ around the forward direction. The whole spectrometer is under control of a table-top calculator (Hewlett-Packard 9825A).

The apparatus has been operated in three different modes; the energy loss spectrum at fixed electron impact energy; the excitation function versus the electron impact energy; the differential cross section versus the scattering angle.

All measurements have been made at constant pass energy. The resolution of the whole spectrometer has been set between 23 and 32 meV, according to the experimental conditions. The calibration of the energy loss scale has been performed using the elastic scattering peak as the zero of the scale.

The variation of the collision volume with scattering angle has been deduced from measurements of the elastic differential cross section of N_2 at 7 eV for angles ranging from 10° to 120° and comparison to the absolute values.[15]

The transmission of the spectrometer in the 4–12 eV electron impact energy range has been obtained by measurement of the elastic differential cross sections in N_2 in this energy range and comparison of these curves with the absolute data.[15,16] The calibration of the incident electron energy

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[b] Maître de Recherches FNRS.

scale has been achieved by observing the $v' = 0$ and $v' = 1$ levels of the nitrogen ${}^2\Sigma_g^+$ Feshbach resonance in the $v'' = 0$ and $v'' = 1$ exit channels of the electronic ground state which are located at 11.48 and 11.75 eV, respectively.[17,18] The accuracy is about 10 meV.

The gas sample was the commercial one from Matheson and Co. The purity claimed by the manufacturer is better than 99%. The gas has been used without further purification.

III. THE METHYLAMINE MOLECULE

Methylamine is a 18 electron molecule and belongs to the C_s symmetry group. It has fifteen fundamental vibrational modes which all are both infrared and Raman active. Nine vibrations are of the A' type whereas the others have A'' symmetry. The corresponding wave numbers (in cm^{-1}), energies (in meV), symmetries, natures and relative intensities in infrared and Raman gaseous spectroscopies are presented in Table I.[19–21]

The methylamine molecule has a ground state permanent dipole moment of 1.23 Debye[22] and a polarizability of 4 Å^3.[23]

The energy ordering of the highest occupied valence molecular orbitals (HOMO) is as follows[24]

$$\ldots\ (5a')^2\ (6a')^2\ (2a'')^2\ (7a')^2\ \tilde{X}\ {}^1A'.$$

The lowest unoccupied molecular orbitals (LUMO) have been predicted by SCF-LCAO calculations to be $8a'$, $3a''$, and $9a'$, respectively.[25,26] However, semiempirical calculations performed by Salahub[27] have led to a A' assignment for the two lowest unoccupied molecular orbitals.

The two lowest optically observed singlet states have been considered as $3s$ and $3p$ Rydberg ones, based on their term values.[28] This assignment has been further supported by inner-shell electron energy loss spectroscopy(1,3) which has succeeded in resolving the $3pa'$ and $3pa''$ terms and suggesting the $3pa'$ to be at lower energy than the $3pa''$ on the basis of Salahub's calculations.[27] The outer-valence-shell electron energy loss spectroscopy and the measurement of the angular differential cross sections have led to A' and A'' assignments for the two lowest energy optically observed singlet excited states corresponding to the most intense transitions.[4] The vibrational pattern of the first singlet band has suggested that the corresponding state is not purely Rydberg in character. Excitation of the second $3p$ orbital has not been resolved in the spectra.

IV. RESULTS

We first report the energy loss spectra of methylamine in the vibrational excitation region corresponding to the $\Delta v = 1,2$ transitions.

Second, the excitation functions of some groups of vibrational modes are presented in the 4 to 12 eV impact energy range.

Finally, we discuss the elastic and vibrational angular differential cross sections obtained at 7.2 eV impact energy.

A. Energy loss spectra

The spectra have been recorded in the energy loss range of 0–1.1 eV, corresponding to the excitation of the fundamental modes and of the first harmonics and combinations.

The spectrum recorded at 30 eV, 30° is shown in Fig. 1. In addition to the elastic peak, it exhibits four bands. First, the band at 116 meV ($\nu_{9,8,7}$) (The notation $\nu_{x,y,z}$ is in relation with the vibrational modes ν_x, ν_y, and ν_z of which frequencies are very close in energy and not resolved within the experimental resolution. It will be used throughout the description of the spectra and the discussion.) which corresponds to the excitation of the NH_2 wagging vibration (ν_9), of the CN stretching vibration (ν_8), and of the symmetric CH_3 rocking vibration (ν_7). The CH_3 and NH_2 deformation modes ($\nu_{5,6,12}$ and ν_4) are present at 181 meV. Excitation of the CH_3 stretching modes ($\nu_{2,3,11}$) is observed at 363

TABLE I. Symmetries, nature of modes, wave numbers (in cm^{-1}), energies (in meV) and relative intensities in infrared and Raman spectroscopies for the fundamental vibrations of the methylamine molecule. W: weak; M: medium; S: strong; VS: very strong.

Symmetry		Nature of the mode	Wave number	Energy	Relative intensities IR (Refs. 20 and 21)	Raman (Ref. 19)
A'	ν_1	NH_2 stretching	3361	417	W	VS
	ν_2	CH_3 stretching	2961	367	VS	VS
	ν_3	CH_3 stretching	2820	350	VS	S
	ν_4	NH_2 scissoring	1623	201	S	
	ν_5	CH_3 deformation	1473	183	S	M
	ν_6	CH_3 deformation	1430	177	M	
	ν_7	CH_3 rocking	1130	140	M	
	ν_8	CN stretching	1044	129	S	S
	ν_9	NH_2 wagging	780	97	VS	W
A''	ν_{10}	NH_2 stretching	3427	425	W	W
	ν_{11}	CH_3 stretching	2985	370	VS	
	ν_{12}	CH_3 deformation	1485	184		
	ν_{13}	NH_2twisting	···	···		
	ν_{14}	CH_3 rocking	1195	148		
	ν_{15}	Torsion	268	33		

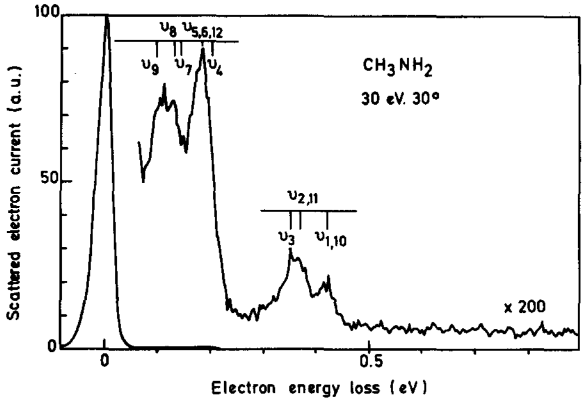

FIG. 1. Vibrational energy loss spectrum recorded at 30 eV impact energy for a 30° scattering angle with a resolution of 32 meV.

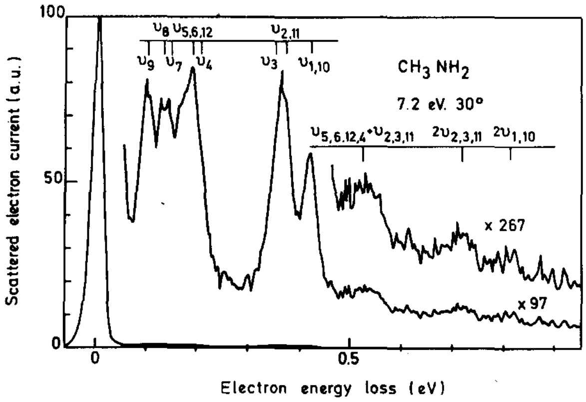

FIG. 2. Vibrational energy loss spectrum recorded at 7.2 eV impact energy for a 30° scattering angle with a resolution of 26 meV.

meV while the NH_2 stretching modes ($\nu_{1,10}$) manifest themselves at the high energy side of the $\nu_{2,3,11}$ band by a incompletely resolved peak located at 418 meV. It should be noted that the torsion mode of frequency 33 meV (ν_{15}) is not observed in our spectra; possibly it might be hidden on the high energy side of the elastic peak. The energy values of the observed features are tabulated in Table II and compared to those obtained by gaseous infrared spectroscopy[20,21] with which they are in good agreement.

The energy loss spectrum recorded at a lower electron impact energy (7.2 eV) and for a 30° scattering angle as displayed in Fig. 2 shows evidence of strong modifications relative to the high impact energy one (Fig. 1). The intensity of the 363 and 418 meV bands due to the CH_3 and the NH_2 stretching vibrational modes, ($\nu_{2,3,11}$ and $\nu_{1,10}$) respectively, increases strongly relative to that of the other ones. Moreover, additional bands are observed at higher energy losses i.e., at 524, 715, and 819 meV (Table II). They are not observed in the high energy spectrum and correspond to the excitation of the combinations between the $\nu_{5,6,12,4}$ and the $\nu_{2,3,11}$ groups, of the harmonics of the CH_3 stretching modes $2\nu_{2,3,11}$ and of those of the NH_2 stretching modes $2\nu_{1,10}$, respectively.

B. Excitation functions of the groups of vibrational modes

The excitation functions for the $\nu_{2,3,11}$, $\nu_{1,10}$, and $\nu_{5,6,12,4}$ groups have been measured at an angle of 30° for impact energies ranging from 4 to 11.5 eV and are displayed in Figs. 3, 4, and 5, respectively.

The relative excitation functions of the CH_3 and NH_2

TABLE II. Energy values (meV) for the observed bands in the 30° spectra recorded at 30 and 7.2 eV.

	Energy loss				
Vibration	at 30 eV	at 7.2 eV	Symmetry	IR (Refs. 20 and 21)	Nature of the mode
ν_{15}	…	…	A''	33	NH_2 torsion
ν_9		99	A'	97	NH_2 wagging
ν_8	116		A'	129	stretching CN
		132			
ν_7			A'	140	
					CH_3 rocking
ν_{14}			A''	148	
ν_6			A'	177	
ν_5			A'	183	CH_3 deformation
	181	181			
ν_{12}			A''	184	
ν_4			A'	201	NH_2 scissoring
ν_3			A'	350	
ν_2	363	364	A'	367	CH_3 stretching
ν_{11}			A''	370	
ν_1			A'	417	
	418	418			NH_2 stretching
ν_{10}			A''	425	
		524			combinations
		715			$2\nu_{2,3,11}$
		819			$2\nu_{1,10}$

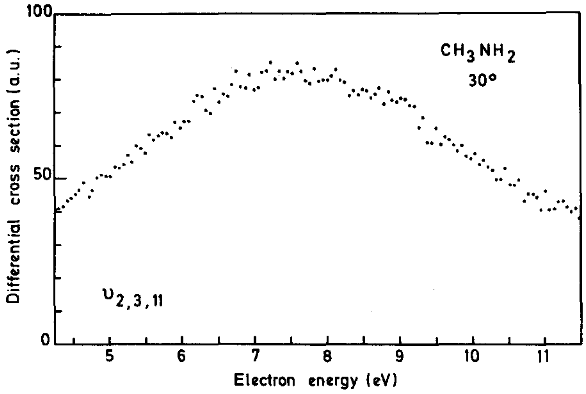

FIG. 3. Relative excitation function of the CH$_3$ stretching vibrational modes $\nu_{2,3,11}$ versus the electron impact energy at 30°.

stretching vibrational modes ($\nu_{2,3,11}$ and $\nu_{1,10}$) exhibit a broad structureless peak (energy width of 4 eV) centered at around 7.5 eV (Figs. 3 and 4). This suggests the excitation of a shape type resonance with a very short lifetime. This is confirmed by the low value for the band intensity ratio of the harmonics of the CH$_3$ and NH$_2$ stretching modes to the fundamental ones (Fig. 2). Since the maxima and the energy widths of the bands are very similar in both excitation functions, the same shape resonance probably leads to the enhancement of these two vibrational excitation functions.

The relative excitation function of the $\nu_{5,6,12,4}$ group also shows a broad structureless band (Fig. 5) which has a maximum at 8.3 eV, thus 0.8 eV higher than for the excitation functions of the stretching vibrations $\nu_{2,3,11}$ and $\nu_{1,10}$. So it seems that another shape resonance located at higher impact energy contributes to the enhancement of the $\nu_{5,6,12,4}$ group cross section in addition to the 7.5 eV one. As the cross section enhancement extends over a large energy range, this resonance too will be very short-lived.

It is also to be noted that these excitation functions are not quite strongly enhanced by the resonance and have a non-negligible contribution from the direct process in addition to the resonant one, roughly of the same order of magnitude (Figs. 3–5).

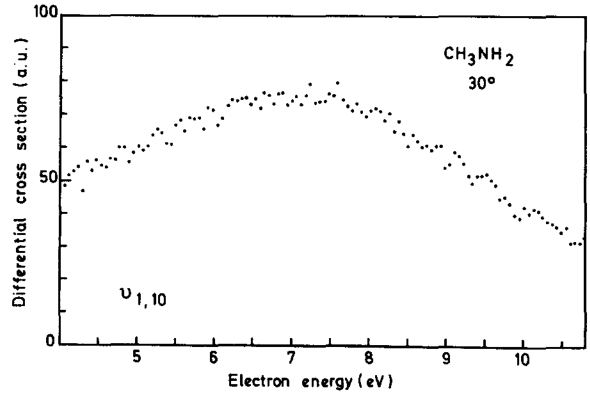

FIG. 4. Relative excitation function of the NH$_2$ stretching vibrational modes $\nu_{1,10}$ versus the electron impact energy at 30°.

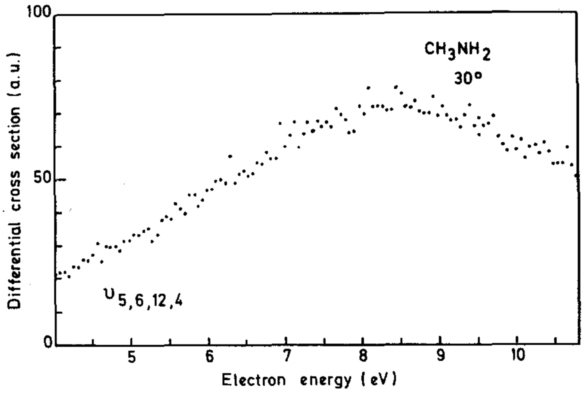

FIG. 5. Relative excitation function of the CH$_3$ and NH$_2$ deformation vibrational modes $\nu_{5,6,12,4}$ versus the electron impact energy at 30°.

C. Relative elastic and vibrational differential cross sections at 7.2 eV impact energy

The vibrationally resolved angular differential cross sections have been determined using the following procedure. First, we have measured the relative elastic angular differential cross section at 7.2 eV for angles ranging from 10° to 120°. Then, on the basis of the energy loss spectra recorded at several angles between 10° and 90°, the inelastic/elastic ratios of the vibrational and elastic scattering peaks have been determined as a function of scattering angle. As these ratios are equal (to a good approximation) to the corresponding cross section ratios, the relative elastic differential cross section has been used together with these intensity ratios to obtain the relative differential cross sections for the vibrational scattering.

The elastic differential cross section is shown in Fig. 6. It diminishes very rapidly from 10° to 40° and less rapidly between 40° and 90°. Above 90°, there is a slight enhancement of the cross section, roughly symmetrical to that between 60° and 90°. This behavior qualitatively agrees with a *p* type outgoing wave of the resonantly scattered electron.

The differential cross sections of the various groups of modes are presented in Fig. 7. They have been normalized to that of the ν_9 vibrational mode at 10°.

The ν_9 differential cross section diminishes very rapidly between 10° and 30°. This behavior is quite similar to that of the ν_2 symmetric deformation mode in NH$_3$ (Ref. 29) for which it is the mode with the largest variation of the dipole moment during the vibration.[30,31] The cross section variation is the largest for this mode, much larger than for the other vibrational modes. That means that the direct process is very likely important in the excitation of the NH$_2$ wagging deformation mode, at least at low angles (below 30°). Above 30°, no information can be obtained due to the vanishing cross section: the band corresponding to the ν_9 mode is no longer resolvable from the other bands, due to its low intensity.

The largest variation of the differential cross section at low angles after that of ν_9 is for $\nu_{2,3,11}$ (Fig. 7). In that case too, the direct process at low angles might have a non-negligible contribution.

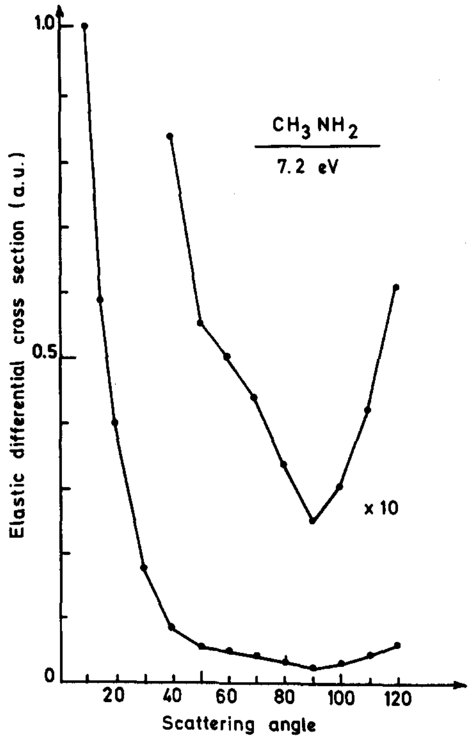

FIG. 6. Relative elastic differential cross section versus the scattering angle at 7.2 eV.

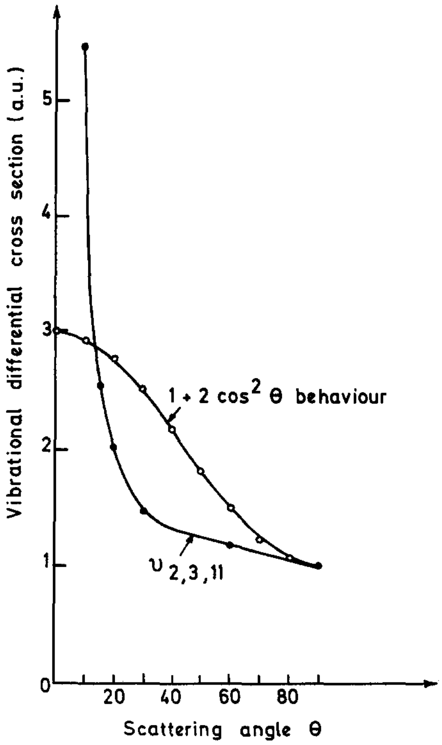

FIG. 8. Comparison between the measured angular differential cross section of the CH_3 stretching vibrational modes $\nu_{2,3,11}$ and the calculated behavior for a $p\sigma$ partial wave (Refs. 32 and 33).

Above 20°, the differential cross sections of the $\nu_{2,3,11}$, $\nu_{1,10}$, $\nu_{8,7}$, and $\nu_{5,6,12,4}$ groups diminish smoothly; they all have roughly the same behavior. As shown on an expanded scale in Figs. 8 and 9 for the $\nu_{2,3,11}$ and $\nu_{1,10}$ modes, respectively, this behavior is compatible with a p type character of the outgoing wave.[32,33] The agreement with a $1 + 2\cos^2\theta$ function is only qualitative and will be discussed hereafter in the frame of the excitation mechanism.

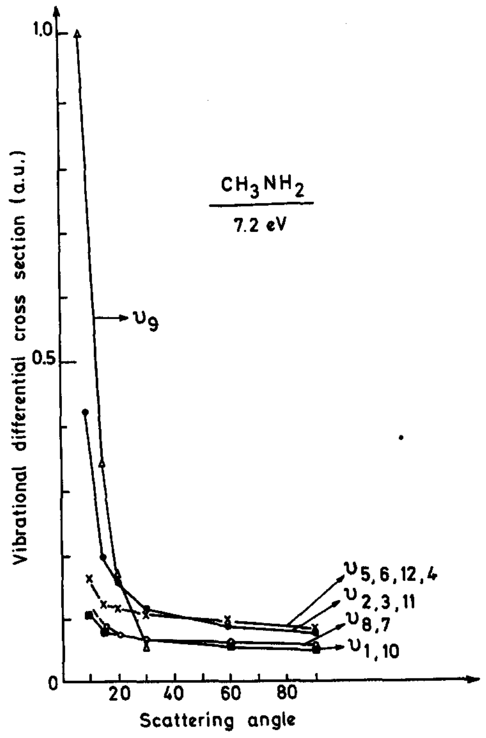

FIG. 7. Relative vibrational differential cross sections versus the scattering angle at 7.2 eV.

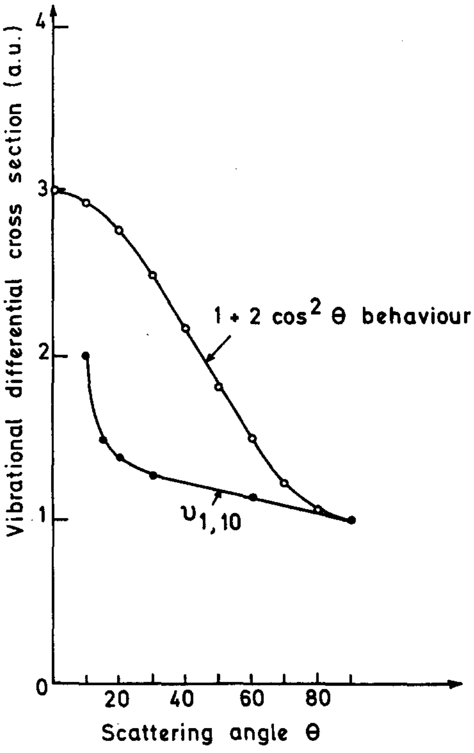

FIG. 9. Comparison between the measured angular differential cross section of the NH_2 stretching vibrational modes $\nu_{1,10}$ and the calculated behavior for a $p\sigma$ partial wave (Refs. 32 and 33).

V. DISCUSSION

The symmetries of the shape resonances will be discussed on the basis of the results reported above. A comparison between NH_3 and CH_3NH_2 will also be made in terms of unoccupied molecular orbitals and ionization energies and of the methyl group role in the substitution.

A. Symmetries of the resonant states

According to the selection rules developed for electron impact resonant vibrational excitation by Wong and Schulz[34] and later reformulated by Gallup,[35] the vibrational modes resonantly excited must have the symmetry of the symmetrized square of the irreducible representation of the resonant state involved. That means that only totally symmetric vibrations will be excited for nondegenerate resonant states. Moreover, vibrations having the symmetry of the resonant state can be excited through a $s\sigma$-wave mechanism, but generally with a less important intensity.[35-37] Application of the first selection rule to the methylamine molecule leads to the prediction that A' vibrational modes will be excited whatever the symmetry of the resonant state i.e., A' or A''. The A'' vibrational modes could be excited via the contribution of a $s\sigma$-wave through a resonant state of A'' symmetry.

1. Symmetry of the 7.5 eV shape resonance

The 7.5 eV shape resonance contributes predominantly to the excitation cross sections of both the CH_3 and NH_2 stretching modes ($\nu_{2,3,11}$ and $\nu_{1,10}$). Both vibration groups may have A' and A'' components separated by a few meV, and not resolvable in our experiments. As shown in Table I, the CH_3 stretching vibrations ν_2 and ν_3 have A' symmetry while ν_{11} belongs to the A'' type. For the NH_2 stretching ones, the ν_1 and ν_{10} modes have A' and A'' symmetries, respectively. So experimentally it is not possible to see evidence of the excitation of the A'' modes in addition to the expected A' ones. However, the selectivity of the resonant vibrational excitation is determined not only by the symmetry selection rules but also by the charge distribution of the additional electron in the unoccupied molecular orbital.[37] In this case, the CH_3 and NH_2 stretching modes being selectively excited, the charge distribution of the additional electron will be predominantly located on the C–H and N–H bonds. Thus the charge distribution is very likely that of the $3a''$ molecular orbital for which SCF-LCAO calculations[25] indicate high selective density on both C–H and N–H bonds. The resonant state then seems to be $^2A''$.

According to the angular correlation considerations made by Read[32] and Andrick and Read,[33] a first allowed $p\sigma$ partial wave and an angular dependence for $f(\theta)$ of $(1 + 2\cos^2\theta)$ are predicted for A' vibronic final states. The angular differential cross sections of the CH_3 and NH_2 stretching vibrations ($\nu_{2,3,11}$ and $\nu_{1,10}$) displayed in Figs. 8 and 9 are compared to the predicted $p\sigma$ partial wave angular dependence.[32,33] We can see that the two curves agree qualitatively but not quantitatively. That confirms the p character of the outgoing wave observed in the elastic angular differential cross section (Fig. 6). The deviation from a pure p character could be due to the presence of additional partial waves in the resonant process associated with the excitation of A' modes. It can also be due to the contribution of the direct excitation process, which is not negligible in the excitation functions of the $\nu_{2,3,11}$ and $\nu_{1,10}$ groups (Figs. 3 and 4). With this hypothesis, only A' vibrational modes are expected to be excited within the frequency groups. This is supported by the fact that no shifts in energy loss are observed for the $\nu_{2,3,11}$ and $\nu_{1,10}$ peaks with the scattering angle.[36]

2. Symmetry of the higher energy shape resonance

This shape resonance manifests itself in the excitation functions of the CH_3 and NH_2 deformation vibrational modes ($\nu_{5,6,12}$ and ν_4). It could be formed by the temporary trapping of the incident electron in the third unoccupied molecular orbital $9a'$, which is mostly located on the C–H bonds.[26] Thus, the resonant state would be of A' symmetry.

B. Comparison between NH_3 and CH_3NH_2

Methylamine is formally formed by the substitution of a hydrogen of ammonia by a methyl group.

In ammonia a Feshbach type resonance is associated with the lowest Rydberg excited state and centered at 5.7 eV. That resonant state decays by dissociative attachment, leading to the formation of the H^- and NH_2^- fragment negative ions.[2,7-10] In methylamine, H^- and CNH_4^- fragment negative ions are known to occur with a maximum at 5.5 eV in the dissociative attachment cross section.[2,7,12] On the analogy to NH_3, these negative ions would be formed by dissociation of a Feshbach type resonance, which would have as parent the first singlet Rydberg state at 5.75 eV.[4] This Feshbach resonance would be partly responsible for the 5.4 eV band observed in the threshold excitation spectrum[13] and would contribute to populating the lowest triplet excited state ($\geqslant 4.75 \pm 0.1$ eV)[2,4] by ejection of zero kinetic energy electrons. In this case, the electron affinity of the Rydberg state would be about 0.3 eV.

The geometrical properties in NH_3 (Ref. 38) and CH_3NH_2 as well as the ionization energies of the two highest energy occupied molecular orbitals are shown in Table III. In NH_3, these latter are the $1e$ and $3a_1$ (n_N) molecular orbitals[39] respectively, whereas in CH_3NH_2 they are the $2a''$ and $7a'$ (n_N) ones.[24]

In ammonia, a shape resonance has been seen centered at 7.3 eV.[11] This consists of the neutral molecule plus an electron in the second unoccupied molecular orbital $2e$.[11,40]

TABLE III. Geometrical and molecular properties of NH_3 and CH_3NH_2.

	Bond lengths (Å)			Ionization energy (eV)		
	NH	CN	CH	$1e$	$2a''$	n_N
NH_3	1.015 (Ref. 38)	···	···	15.80 (Ref. 39)		10.90 (Ref. 39)
CH_3NH_2	1.0096 (Ref. 22)	1.4714 (Ref. 22)	1.0987 (Ref. 22)		13.22 (Ref. 24)	9.64 (Ref. 24)

In methylamine, a shape resonance centered at 7.5 eV is formed by the capture of the incident electron in the second unoccupied molecular orbital $3a''$.

So, it is interesting to establish a correlation diagram (Fig. 10) for the ionization energies of the two highest occupied molecular orbitals and for the energies of the shape resonances observed in both molecules. In this diagram are also shown the term values associated with the second unoccupied molecular orbitals populated by 1*s* nitrogen and 1*s* carbon electronic transitions.[3] For methylamine, we have used the term values associated with the second unoccupied orbital which has been assigned by Sodhi and Brion[3] to the $3pa'$ one on the basis of Salahub's calculations. However, the present data suggest that the symmetry of the second unoccupied orbital is A'', in agreement with the calculations of Fink and Allen.[25] This conclusion also agrees with the outer-valence-shell electron energy loss spectroscopy,[4] which has led to A' and A'' assignments for the two optically most intense transitions $7a'(n_N) \rightarrow 3sa'$ and $7a'(n_N) \rightarrow 3pa''$, respectively. The second 3*p* Rydberg state of A' symmetry is not resolved in the electron energy loss spectra. The stabilization energies of these orbitals between the electron–molecule and electron–molecular ion systems can be obtained by summing the respective term values and energies of the shape resonances.[41] They are very similar for NH_3 and CH_3NH_2 molecules (10.53 and 10.48 eV, respectively). Thus, substitution of an H atom of NH_3 by the CH_3 radical involves a weak destabilization in energy of the second unoccupied molecular orbital (Fig. 10).

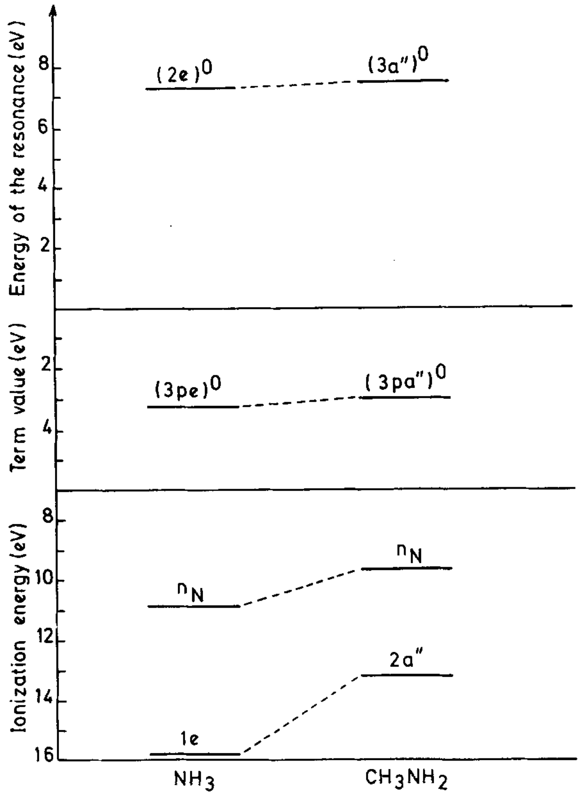

FIG. 10. Correlation diagram for the ionization energies of the two highest energy occupied molecular orbitals and for the energies of the shape resonances in NH_3 and CH_3NH_2.

VI. CONCLUSIONS

Vibrational excitation of the normal modes of methylamine has been studied by low energy electron impact. Electron energy loss spectra have been recorded at 30 eV and at 7.2 eV. The excitation functions of the methyl and amine stretching modes have been measured in the 4 to 11.5 eV impact energy range. They are shown to be enhanced by a resonance centered at 7.5 eV. This latter has been interpreted in terms of a short-lived resonance in the context of the angular momentum associated to an A'' orbital. The relative angular differential cross sections for the elastic scattering and the vibrational modes have been reported at the resonance energy. They all suggest a *p* character for the resonant outgoing wave. The excitation function of the methyl and amine deformation modes is enhanced by a resonance located at higher energy ($\geqslant$8.3 eV) and related to an A' short-lived resonance.

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