International Journal of Mass Spectrometry 277 (2008) 240–244

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Vibrationally resolved EELS at the liquid surface of hydroxypropionitrile

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ARTICLE INFO

Article history:
Received 28 March 2008
Received in revised form 20 May 2008
Accepted 20 May 2008
Available online 28 May 2008

Dedicated to Prof. Eugen Illenberger at the occasion of his 65th birthday.

Keywords:
Vibrationally resolved electron energy loss spectroscopy

ABSTRACT

We have applied the technique of EELS (=electron energy loss spectroscopy) to the liquid surface of 3-hydroxypropionitrile. Even though the presence of the vapor deteriorates the performance of the spectrometer, the resolution is sufficient to separate the vibrational stretch modes of the three groups OH, CH, CN. The energy dependence allows to identify non-resonant and resonant excitation mechanisms. Comparison to gas phase results, measured in the same apparatus, leads to a surprising difference in the excitation of the CN group. The different environment in the liquid and gaseous phase appears to strongly influence the character of the electronic resonance state.

1. Introduction

Electron energy loss spectroscopy is a well established tool for the characterization of solid surfaces [1]. In particular the identification of vibrational modes of adsorbed molecules, referred to as HREELS (high resolution electron energy loss spectroscopy), is a widely applied technique [2,3]. The energy resolution has been improved by Ibach to $\Delta E \leq 0.5$ meV [4], thus almost competing with the resolving power of IR spectroscopy applied to surfaces (IRAS, i.e., IR reflection absorption). It is obvious that the understanding of liquid surfaces could benefit from electron energy loss spectroscopy as well. Indeed, the technique has been employed by Ballard et al. already about two decades ago [5]. However, this study had to consent itself with an energy resolution of 1 eV which is good enough to discern different electronic excitations, but vibrational spectroscopy could not be carried out. The same holds for later work from our group [6]. The first EELS study to show vibrational excitation at a liquid surface was carried out about a decade ago [7]. The energy resolution of $\Delta E \leq 75$ meV was sufficient to make vibrational excitation visible, but the signal from different groups could not be separated. The first successful attempt in that respect was published last year [8]. The liquid studied was glycerol which lends itself to the investigation by vacuum based techniques due to its low vapor pressure. The present study is devoted to the application of vibrationally resolved EELS at the liquid surface of 3-hydroxypropionitrile. This liquid lends itself to a study by electron spectroscopy due to its moderate vapor pressure [9]. The energy resolution of the apparatus under UHV conditions is $\Delta E = 12$ meV, while the presence of the liquid and its vapor reduces the resolution to $\Delta E = 25$ meV in spite of differential pumping of the electron gun as well as of the electron spectrometer.

It is well known that slow electrons can excite molecular vibrations via two different mechanisms, the dipole mechanism and the resonance mechanism. In the first case, the varying electric field of the passing electron causes the excitation with the dipole being the leading moment. In the second case, the incident electron in captured into a resonance state thus modifying the interaction potentials within the molecule. After reemission of the electron the molecule may remain in a vibrationally excited state. Even though direct impact of an electron is not able to change the momentum distribution of atoms, the term impact collision has been introduced into the literature in the context of vibrational excitation at metallic surfaces [10]. The authors state clearly, however, that the mechanism involves the transient population of resonance states at the surface. In the present paper, we discern only two mechanisms, dipole and resonance mechanisms.

At atomically flat solid surfaces the two mechanisms are distinguishable via their angular dependence. The dipole mechanism shows a significant peak in specular direction while the resonance mechanism does not have a memory of the direction of the incident electron beam. At liquid surfaces this distinction vanishes as discussed before [7]. Thus, the distinction between both mechanisms has to rely on studying the influence of the primary energy. In the previous [8] and in the present study this strategy is carried through.

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1387-3806/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.ijms.2008.05.028

When identifying a resonance that leads to vibrational excitation one may ask whether additional decay channels exist. One of the most extensively studied channel is fragmentation of the molecule into two or more parts one of which is negatively charged. This is the field of dissociative attachment that has been successfully studied over several decades by Eugen Illenberger and his co-workers, first in the gas phase and later on at the surface of the condensed phase as well. In the present communication we will show that in the field of vibrational excitation the comparison between gas phase and condensed phase (in our case liquid phase) leads to interesting results. Further, we find that the resonance leading in OH-containing molecules to the emission of OH^--fragments (DA) is positioned in the same energy interval as the resonance leading to vibrational excitation. It may be safe to conclude that the picture of one common resonance with two different decay channels is justified.

The paper is organized as follows. In the third section we present our experimental findings on vibrationally resolved EELS at gaseous and liquid 3-hydroxypropionitrile (HPN). In the fourth section we compare the identified resonance for OH(ν) excitation in glycerol from the previous paper [8] with data from dissociative attachment at a similar molecule and we present a surprising finding on the behavior of CN(ν) excitation in the gaseous and the liquid phase. We propose a tentative explanation.

2. Experimental

2.1. Material

3-Hydroxypropionitrile has been purchased from FLUKA, the stated purity being >99%. The color is yellowish which is indicative for impurities. The purchased material has been purified by distillation. The procedure was repeated several times. The liquid is then clear and colorless. The surface tension has been determined via the Wilhelmy plate method to be $\sigma = 51.40$ mN/m at −6 °C, while the density was measured to be $d = 1.0453$ g/cm^3 at 20 °C. Further tests by ^{1}H NMR showed that the intensity of unidentified signals decreased with every distillation step, but did not vanish entirely.

2.2. EELS apparatus

The apparatus used to perform the EELS experiments has been described before [8]. Therefore only a brief statement follows here. A UHV setup manufactured by the company SPECS contains the differentially pumped electron source which is a modified version of the Delta 0.5 HREELS device by SPECS. The electron energy can be varied from 0.1 eV to 200 eV. The analyzer is differentially pumped as well. It is the PHOIBOS 100-MCD5 hemispherical analyzer manufactured by SPECS. At a primary energy of 20 eV, the spatial width of the primary electron beam was found to be ±1.2°. The energetic width of the primary beam at pass energy of 2.5 eV at the analyzer entrance was equal to 21 meV. This value is sufficiently small to resolve the loss signals due to the O–H and C–H stretching vibrations.

The electron source including its vacuum chamber can be rotated. If the direction into the spectrometer is taken to be 0° then the range of rotation is −40° to 120°. The liquid target can be rotated as well. Thus, the direction of the incident beam and the direction of the reflected electrons can be set independently with respect to the surface normal.

The base pressures in the main chamber, in the chamber of the electron gun and in the analyzer chamber are several 10^{-9} mbar in the absence of a liquid. The presence of the liquid leads to an increase of the pressure in the main chamber to several 10^{-5} mbar. The pressures in the differentially pumped chambers are less affected by about one order of magnitude.

The liquid is contained in a reservoir made of stainless steel. A stainless steel disk is immersed into the liquid and continuously rotated by a motor, leading to the formation of a thin liquid film on the disk of some tenths of a millimeter. The rotation of the disk provides a continuous regeneration of the liquid surface. When the disk emerges from the reservoir, a skimmer scrapes the surface of the liquid film on the disk. The skimmer removes slowly adsorbing impurities such as hydrocarbons. Hence, a clean surface is created. The temperature of the reservoir is measured with a platinum resistor thermometer and controlled by a cryostat.

3. Results

3.1. HPN in the gas phase

The EELS measurements of gas phase HPN have been carried out under forward scattering geometry as the intensity turned out to be very low under larger scattering angles. In this geometry the elastic peak is too intense to be measured under the same conditions, therefore it has been recorded at a finite scattering angle in order to get the primary energy for reference in any run. The three stretch vibrations could be identified at energies of 459 ± 3 meV (OH), 370 ± 3 meV (CH) and 297 ± 4 meV (CN), cf. Fig. 1. The quoted uncertainties reflect the standard deviation of the energy losses from measurements at different primary energies. Intensity variations of the primary beam did not allow to refer the intensity of the loss peaks to the intensity of the elastic peak. Thus, our gas phase data as function of primary energy are presented after normalization to the sum of the three loss peaks OH, CH, CN. The relative probability for CN excitation passes through a broad maximum peaked near 10 eV (Fig. 2).

3.2. HPN in the liquid phase

The liquid sample has been cooled to −6 °C in order to reduce the vapor pressure. The liquid is still well above its melting point at −17 °C. The same three molecular groups have been identified in EELS from the liquid surface of HPN. The vibrational quanta are shifted to smaller values compared to the gas phase: OH (422 ± 7 meV), CH (364 ± 5 meV), CN (280 ± 2 meV). Again the standard deviation is evaluated from measurements with different

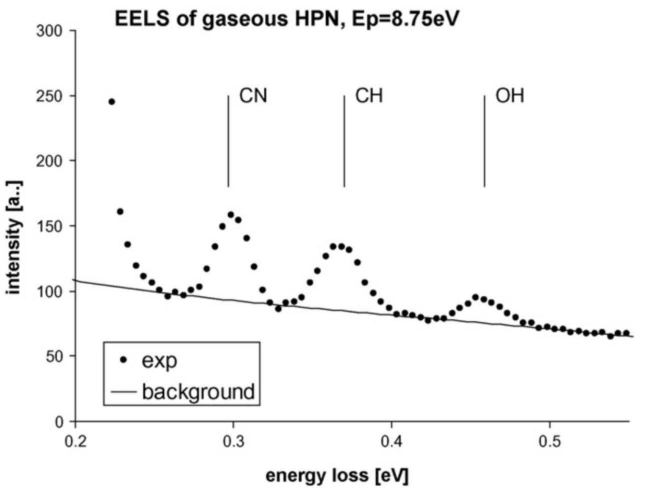

Fig. 1. Vibrationally resolved EELS of gaseous 3-hydroxypropionitrile for an electron energy of 8.75 eV.

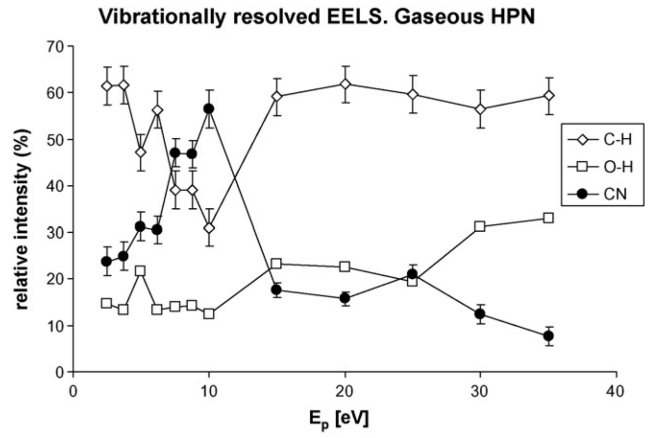

Fig. 2. EELS of gaseous 3-hydroxypropionitrile. Energy dependence.

primary energy between 2.5 eV and 35 eV. IR data taken from liquid HPN confirm the values within the quoted error bars.

The angular dependence of the signal has been studied in two ways. Firstly, the reflected electrons were measured in specular direction with the angle of incidence being varied between 5° and 55° against the surface plane. It is interesting to note that grazing incidence below 10° yields a shift of the energy losses to larger values. In particular the OH mode displays vibrational quanta which are typical for the gas phase. Apparently, in this scattering geometry the electrons have a trajectory which enables sufficient contact with vapor to noticeably influence the measurement. At steeper angles of incidence this effect appears to be negligible as evidenced by the agreement between EELS data and IR data taken from a liquid sample, see above. Secondly, we have studied the effect of measuring the energy loss spectrum outside the specular direction. The intensity does vary, but no information could be obtained that did shed any light onto the mechanism of vibrational excitation. The data presented here are taken under specular condition, the angle between direction of incidence and surface plane being 50°.

The peak positions of the three vibrational modes as function of the primary energy are plotted in Fig. 3. The intensity of the three peaks normalized to the elastic signal is plotted in Fig. 4a. For better comparison with the gas phase data, we have included a plot of the relative intensities in Fig. 4b.

The result is surprising: while the CN vibration shows a resonance behavior around $E_p = 10\,\text{eV}$ in the gas phase, this process vanishes in the liquid phase within experimental uncertainty in the range of primary energies between 3 eV and 20 eV. For reference, the two spectra at $E_p = 2.5\,\text{eV}$ and $E_p = 3.75\,\text{eV}$ are shown in Fig. 5. It has been explained already before, that the vapor cannot be a cause for this unexpected behavior.

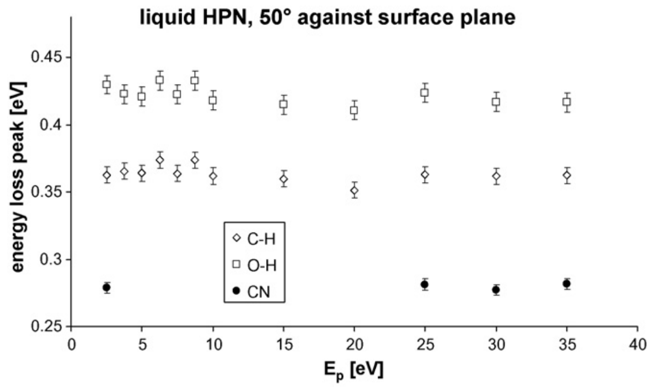

Fig. 3. EELS of liquid 3-hydroxypropionitrile. Energy dependence of peak positions.

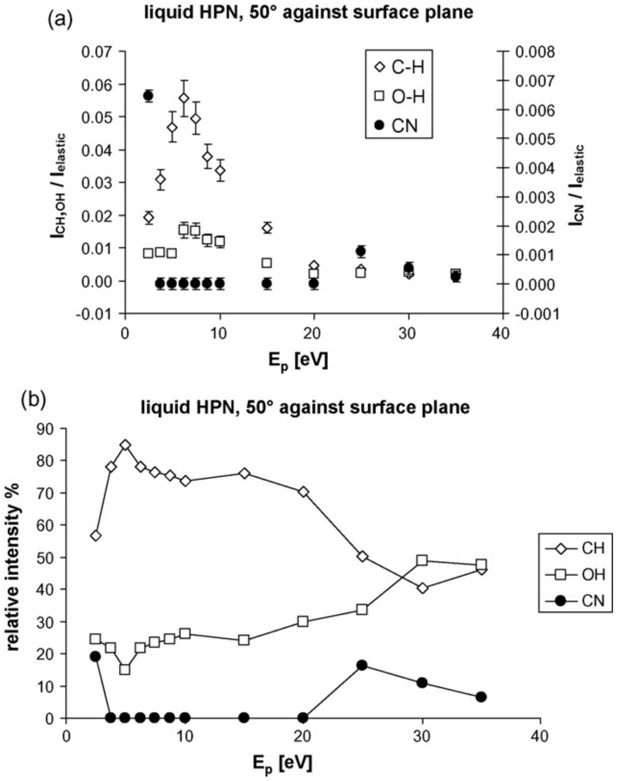

Fig. 4. (a) EELS of liquid 3-hydroxypropionitrile. Energy dependence of intensity. (b) EELS of liquid 3-hydroxypropionitrile. Energy dependence of relative intensity.

4. Discussion

We begin by addressing the EELS data on glycerol from our previous paper [8]. The probability for OH and CH vibrational excitation passes through a local maximum as function of the electron energy. Fig. 6 shows the OH-data together with a fit of the expression

$$\frac{I^{\text{OH}}_{\text{nonres}}}{I_{\text{elastic}}} = \frac{a}{E_{\text{p}}{}^{n}} \tag{1}$$

to the non-resonant contribution. The parameter a and n are empirical constants. The best fit to the data below $E_p = 6.25\,\text{eV}$ and above $E_p = 25\,\text{eV}$ is obtained for $a = 0.085$ and $n = 0.55$. The resonant contribution is then obtained via

$$\frac{I^{\text{OH}}_{\text{res}}}{I_{\text{elastic}}} = \frac{I^{\text{OH}}_{\text{exp}}}{I_{\text{elastic}}} - \frac{I^{\text{OH}}_{\text{nonres}}}{I_{\text{elastic}}} \tag{2}$$

which plotted as well in the figure.

The resonance lies in the same range of energies found for dissociative attachment of another OH containing compound, namely ethanol, by Illenberger and co-workers [11]. The authors report on the energy dependence for formation of several negative fragments in the gas phase and from a thin film of condensed matter. The energy range observed for the condensed phase is shifted slightly against the gas phase data [11] and fits the resonance in Fig. 6 very well. Thus, we may conclude that vibrational excitation of the OH group and dissociative attachment can be conceived to be decay channels of the same resonant state. Further, the resonance involving the OH group appears to exist in both, gaseous and condensed, phases. Only the energetic position seems to be slightly shifted [11]

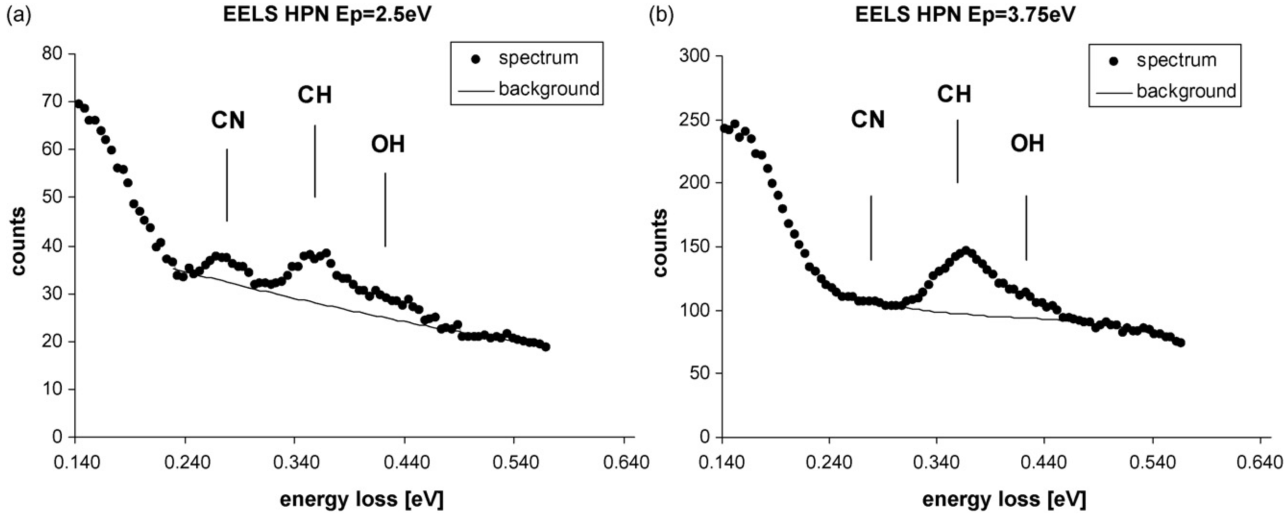

Fig. 5. (a) EELS of liquid 3-hydroxypropionitrile at an electron energy of 2.5 eV. (b) EELS of liquid 3-hydroxypropionitrile at an electron energy of 3.75 eV.

which is easily explained as consequence of changing the environment.

Now, we inspect our results for CN vibrational excitation in hydroxypropionitrile. In the gas phase, we observe an enhancement of the signal between 3 eV and 15 eV of primary energy, cf. Fig. 2. For comparison, it would be interesting to consult other work on gas phase collisions between slow electrons and CN containing molecules. Heni and Illenberger have studied dissociative attachment to several CN containing molecules (saturated nitriles, acrylonitrile and benzonitrile) in the gas phase [12]. The fragment CN^- has been found in the range between 2 and 4 eV and again between 6 and 12 eV. Electron attachment to gas phase acetonitrile has been reported by Sailer et al. [13]. Near $E_p = 3$ eV they find a strong signal of the fragment CH_2CN^- while CN^- is formed around 2 eV and in the interval between 6 and 9 eV. Studies on HPN have not been published. Another study of dissociative attachment to a CN containing molecule has been published recently by Illenberger et al. [14]. They find the fragment CN^- for primary energies in the range from 1 eV to 14 eV in spite of several competing decay channels. We conclude that CN containing molecules display resonances in the energy range between 3 eV and 15 eV for which we observe enhanced excitation of the CN stretch mode in HPN. Thus, the notion that dissociative attachment and vibrational excitation may be conceived as different decay channels of the same resonance can be maintained for the gas phase.

As far as OH and CH groups are concerned, we have stated above that the change from the gas phase to the condensed phase has only a mild influence on the energetic position, but not on the existence of a resonance. In case of the CN group we find a remarkably different behavior. Vibrational excitation of CN is suppressed for the liquid state in a large energy range which includes the range of the gas phase resonance, cf. Fig. 2 and Fig. 4. Again, it would be of interest to compare with other work. HREELS of a frozen, amorphous thin film of acetonitrile adsorbed on Pt substrate has been carried out for primary energies between 2.5 eV and 15.5 eV [15]. All other vibrational modes show little dependence on E_p, while the CN stretch vibration is of comparable intensity only at $E_p = 2.5$ eV, but drops to small values at higher energy.

In our data, the excitation of the CN stretch vibration vanishes within experimental uncertainty, while in the data from ref.15 the signal gets much smaller above $E_p = 3.5$ eV, but retains a finite value. It may well be that a better signal to noise ratio in the vapor free environment of ref. [15] causes this difference. Still, it seems that the observation common to both studies consist in the fact that the CN signal is strong near 3 eV, but vanishes or is distinctly reduced at higher energies, cf. Fig. 7.

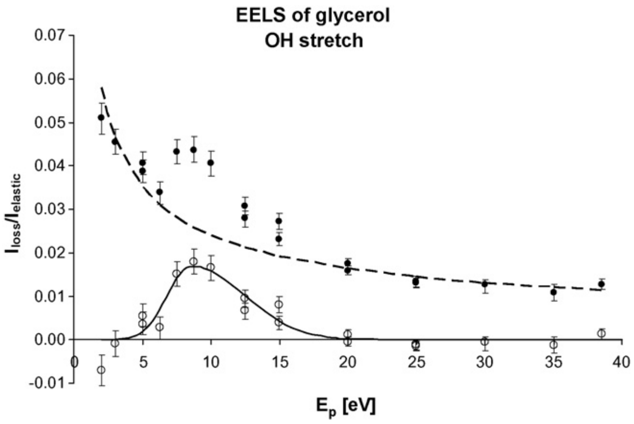

Fig. 6. EELS of liquid glycerol. OH($\nu = 1$) excitation as function of primary energy. Data are from ref. [8]. Dashed line: fit to the non-resonant contribution according to Eq. (1). The open circles represent the resonant contribution as difference between experimental data and the fitted line. The full line is meant to guide the eye.

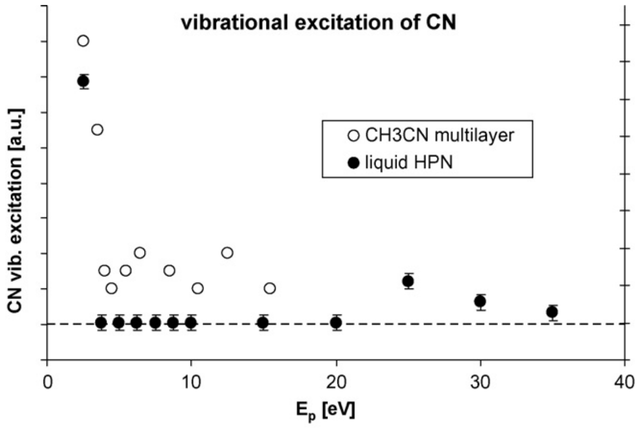

Fig. 7. Vibrational excitation of the CN group by EELS. The open circles represent the data from ref. [15], taken from a multilayer of acetonitrile, the dots are the data from Fig. 4a.

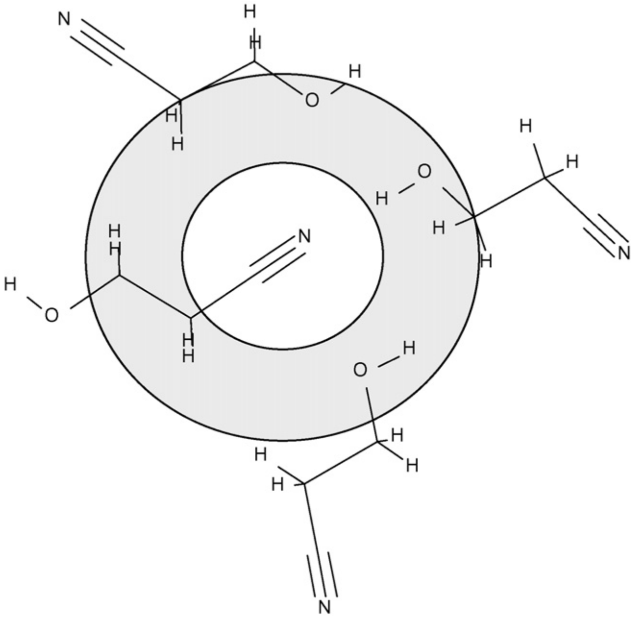

Fig. 8. Scheme of an electronic state in liquid HPN that is centered at the CN group but avoids contact with its center due to high angular momentum.

In ref. [15] the interpretation refers to the strong signal near E_p = 3 eV. Quite naturally, the author relates this signal to the resonance near 3 eV reported for the gas phase by Sailer et al. [13]. Consequently, the energy range above 3 eV does not require any particular consideration.

However, inspecting our data, one is confronted with a somewhat different problem due to the larger range of energies being studied. The CN signal is strong at 2.5 eV, goes down at higher energies, but then recovers above 20 eV. This latter feature is hardly explained by the resonance near 3 eV. Thus, one is attempted to ask a different question, namely which mechanism suppresses the CN signal in the large energy range between 3.75 eV and 20 eV? At present, we can only speculate. We state that the suppression of CN excitation goes along with a resonantly enhanced excitation of the OH and CH groups, cf. Fig. 4. Thus, we have to conceive a transient electronic state that accepts the incident electron which has the property to systematically avoid contact with the CN group but to influence the motion of the other two groups. A planetary type of electronic state could be the answer: the CN group acts as center of attraction that temporarily binds the electron into a state with high angular momentum. The strong dipole moment of the CN group may be conceived to represent a sufficiently strong center of attraction [16,17]. A schematic drawing of this situation is shown in Fig. 8. The nature of this electronic state need not be best described by a time independent orbital. In contrary, it may well be that the electronic motion in such a state is not fast compared to nuclear motion. Thus, the Born Oppenheimer approximation may not be applicable. Then, the picture of an excess electron jumping from site to site may be more appropriate. The situation of excess electrons being transferred between different sites has been treated by Simons and co-workers, e.g., he has studied free electrons of a few eV kinetic energy being captured into temporary states of a peptide, which are subsequently transferred between different molecular sites in order to finally end up breaking a disulfide bond [18].

5. Outlook

In general, we employ particle spectroscopies in order to characterize the properties of liquid surfaces [19,20]. In doing so, we rely on our understanding of the interaction between charged particles like electrons and ions with the liquid state of matter. In the present case, we have come across an experimental result that has forced us to reconsider the behavior of electrons in condensed matter. Further experimental studies and cooperation with theoretical groups will be necessary to solve the question raised at the end of this contribution.

Acknowledgments

We gratefully acknowledge financial support by the Bundesministerium für Bildung und Forschung and by the Deutsche Forschungsgemeinschaft. Petra Swiderek has acquainted us with the PhD thesis by C. Jäggle.

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