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Low energy (0–4 eV) electron impact to N_2O clusters: Dissociative electron attachment, ion-molecule reactions, and vibrational Feshbach resonances

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Electron attachment to clusters of N_2O in the energy range of 0–4 eV yields the ionic complexes $[(N_2O)_nO]^-$, $[(N_2O)_nNO]^-$, and $(N_2O)_n^-$. The shape of the ion yields of the three homologous series differs substantially reflecting the different formation mechanisms. While the generation of $[(N_2O)_nO]^-$ can be assigned to dissociative electron attachment (DEA) of an individual N_2O molecule in the target cluster, the formation of $[(N_2O)_nNO]^-$ is interpreted via a sequence of ion molecule reactions involving the formation of O^- via DEA in the first step. The nondecomposed complexes $(N_2O)_n^-$ are preferentially formed at very low energies (below 0.5 eV) as a result of intramolecular stabilization of a diffuse molecular anion at low energy. The ion yields of $[(N_2O)_nO]^-$ and $(N_2O)_n^-$ versus electron energy show sharp peaks at the threshold region, which can be assigned to vibrational Feshbach resonances mediated by the diffuse anion state as already observed in an ultrahigh resolution electron attachment study of N_2O clusters [E. Leber, S. Barsotti, J. Bömmels, J. M. Weber, I. I. Fabrikant, M.-W. Ruf, and H. Hotop, Chem. Phys. Lett. **325**, 345 (2000)]. © *2010 American Institute of Physics*. [doi:10.1063/1.3505143]

I. INTRODUCTION

Electron attachment to single N_2O molecules has already been extensively studied since the 1960s.[1–4] In these early experiments, the O^- signal arising from dissociative electron attachment (DEA) showed an intense low energy feature with a maximum at 2.3 eV. In most experiments, the O^- signal appeared already at 0 eV. On the other hand, the well established thermochemical data $[D(N_2-O)=1.72$ eV and $EA(O)=1.46$ eV (Ref. 5), see Table I] predict the threshold energy for DEA as 0.26 eV. This seeming discrepancy was largely resolved by Chantry[6] who measured the O^- signal at different gas temperatures in the range from 160 to 1040 K. At room temperature, he observed a single peak with a maximum at 2.3 eV and a small shoulder around 1 eV. At higher temperatures the low energy signal increases dramatically finally resulting in a pronounced peak near 0 eV. These results were later confirmed at improved energy resolution by Brüning *et al.*[7]

The dramatic temperature dependence was interpreted[8] by introducing two different N_2O^- states: a $^2\Sigma$ state at a vertical attachment energy of 2.3 eV and a $^2\Pi$ state at 1 eV. N_2O is linear and isoelectronic to CO_2 but belongs to a different symmetry point-group. Like in CO_2, the anion is bent at an angle of about 130°. The potential energy of the $^2\Pi$ state was considered to minimize at a bending angle of 130° for all N_2-O separations. The observed variation in DEA with temperature was then explained by population of vibra-

tionally excited states of the v_2 bending mode of the linear ground state N_2O, thus giving access to Franck–Condon transitions close to the crossing between the neutral and anionic potential energy surface.

Although subsequent measurements of the O^- angular distributions[9] and vibrational excitations in N_2O (Ref. 10) supported the above interpretation, *ab initio* calculations[11] as well as electron energy loss measurements,[12] however, placed the energy of the $^2\Sigma$ state below that of the $^2\Pi$ state. It thus appears that the characterization of the shape resonance(s) in low energy DEA to N_2O is not completely resolved so far.

Recently, Allan and Skalicky[13] studied the scattering behavior observing strong vibrational excitation of all three normal modes in the threshold region. The effective vibrational excitation at low energies was interpreted to occur via vibrational Feshbach resonances (VFRs) mediated by a diffuse state of the anion where the extra electron is loosely bound by polarization and dipole forces. Sharp peaks on the O^- yield were also observed above the threshold for O^- formation (0.2–0.6 eV) at a spacing reflecting the bending vibration in N_2O. Apparently, the mechanism of DEA to N_2O at low energy is more complex than a transition to a repulsive surface of the anion. The peaks in the O^- yield indicate that VFRs contribute to fragment ion formation, acting as *doorways* to DEA via coupling to the dissociation continuum. On the other hand, a time-of-flight (TOF) analysis of O^- ions formed from single N_2O indicates that the decomposition of the transient negative ion into O^-+N_2 in the en-

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TABLE I. Thermodynamic data relevant in the present study (Refs. [5], [24], and [25]).

Standard heat of formation, ΔH_f^e (eV)	
N_2O	0.85
NO	0.94
NO_2	0.34
O^-	1.12
Electron affinity (eV)	
N_2O	0.22 ± 0.1
NO	0.026
O	1.46
Bond dissociation energy (eV)	
$D(N_2-O)$	1.72
$D(N-NO)$	4.93

ergy range of 1–3 eV is repulsive as obvious from the doublet in the TOF spectrum pointing to translational energy of about 200 meV for the O^- ion.[7] As we shall demonstrate here, VFRs carrying signatures of all three vibrational modes of N_2O are visible on the ionic products $[(N_2O)_nO]^-$ and $(N_2O)_n^-$ arising from electron attachment to N_2O clusters.

In condensed N_2O at cryogenic temperatures, charge trapping (CT) and also electron stimulated desorption of O^- were studied. The CT cross section exhibits a pronounced low energy peak with a maximum near 1 eV at an absolute value of 3.5×10^{-16} cm^3 (Ref. [14]), which represents an enhancement of more than a factor of 35 over the gas phase DEA cross section at room temperature. O^- desorption, on the other hand, is completely restricted to higher energies due to the energetic constraints in ion desorption.[15,16] Electron transmission experiments through thick films of N_2O (>100 ML) spontaneously acquire a surface potential of as high as 5 V, which was explained by spontaneous dipole alignment.[17]

Electron attachment to clusters of N_2O was first studied by Klots and Compton[18] and by Knapp *et al.*[19] at comparatively poor energy resolution. These early studies showed the formation of products of the form $[(N_2O)_nO]^-$ (Ref. [18]) and the nondecomposed anions $(N_2O)_n^-$, $n \geq 1$ (Ref. [19]) with ion yields shifted to lower energies compared to O^- from free N_2O. Recent experiments at appreciably improved energy resolution[20] documented the continuous red-shift of the resonance maximum of the product $[(N_2O)_nO]^-$ with cluster size from 2.58 eV (n=0) to 1.70 eV (n=7). Finally, a study at ultrahigh resolution (1 meV, laser photoelectron attachment) revealed sharp structures in the energy range between 0 and 180 meV observed for products of the form $[(N_2O)_nO]^-$ and also for the nondecomposed anions $(N_2O)_n^-$.[21] These structures were identified as VFRs involving symmetric stretch and bending vibrations. They are significantly red-shifted with the size of the observed cluster ion as a result of the increasing binding energy of the excess electron.

In the present contribution, we present a comprehensive

study on electron attachment to N_2O clusters in the electron energy range from 0 to about 4 eV yielding the DEA products $[(N_2O)_nO]^-$ and $[(N_2O)_nNO]^-$ and the nondecomposed anions $(N_2O)_n^-$ including the monomer N_2O^-.

II. EXPERIMENTAL

Electron attachment to N_2O clusters is studied by means of the high resolution attachment spectrometer described previously.[22,23] In brief, the cluster beam is formed by expansion of pure N_2O through a nozzle of 20 μm diameter into vacuum at variable temperatures (220–300 K) and pressures (2–5 bar). The electron beam is formed in a custom built hemispherical electron monochromator, operated at an energy resolution of 90–120 meV (full width at half maximum) and an electron current of 5–8 nA. Negative ions formed in the collision zone are extracted by a weak electric field toward the entrance of the quadrupole mass spectrometer. The mass-selected negative ions are detected by a channel electron multiplier using a single pulse counting technique. The intensity of a particular mass-selected negative ion is then recorded as a function of the electron energy. Energy calibration is performed using the well known resonance in CCl_4 generating Cl^-. The background pressure during the experiments is in the range of 10^{-7} mbar measured via an ionization gauge at one of the flanges. Hence, we have single collision conditions although weak contributions from ion-molecule reactions directly in the beam cannot completely be ruled out.

III. RESULTS AND DISCUSSION

From all the previous experiments considered in Sec. I,[1–4,6–13] it is well established that DEA to gas phase N_2O yields O^- as the only observable ionic product with a prominent low energy resonance and a maximum in the ion yield near 2.5 eV. In going to clusters, the products $[(N_2O)_nO]^-$, $[(N_2O)_nNO]^-$, and $(N_2O)_n^-$ are observed. As an overview, Fig. 1 shows a representative member of each of the three series indicating that the underlying energy dependences are substantially different, a fact which was not obvious from the previous investigations performed at poor electron energy resolution. The intensity ratio between $[(N_2O)O]^-:[(N_2O)NO]^-:(N_2O)^-$ is roughly 1000:10:1 at an electron energy around 2 eV.

The most abundant ions $[(N_2O)_nO]^-$ can be considered to arise from electron capture by an individual molecule of the target cluster, creating the fragment O^- via DEA. This reaction may be accompanied by evaporation of neutral N_2O units finally resulting in the ionic complexes $[(N_2O)_nO]^-$ (solvated fragment anions). Thus, one expects an ion yield similar to that of O^- from isolated N_2O modified by the respective environment. The second homologous series $[(N_2O)_nNO]^-$ cannot be associated to DEA as NO^- is not generated from single N_2O and would require cleavage of the appreciably strong N–NO bond (4.93 eV, see Table I). Rather, these ionic complexes result from ion molecule reactions within the cluster leading to stable neutral molecules
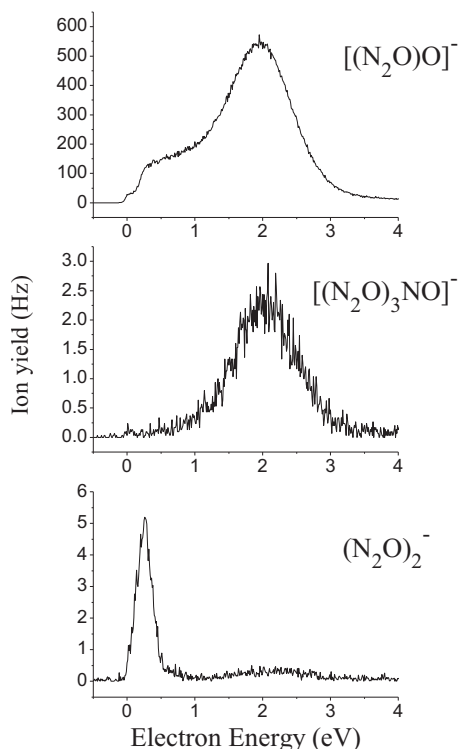
FIG. 1. Ion yields of $[(N_2O)O]^-$, $[(N_2O)_3NO]^-$, and $(N_2O)_2^-$ as representative examples of the three series of ionic complexes observed in electron attachment to N_2O clusters (stagnation pressure of 3 bar and nozzle temperature of 220 K).

(see below). The nondecomposed ions $(N_2O)_n^-$ are finally the result of electron capture by a cluster followed by intramolecular relaxation, thereby evaporating part of the target cluster.

A. Formation of the products $[(N_2O)_nO]^-(n \geq 0)$

Figure 2 shows O^- formation from free N_2O molecules and a few members of the series $[(N_2O)_nO]^-$ including O^- (n=0) generated from clusters. The maximum in the ion
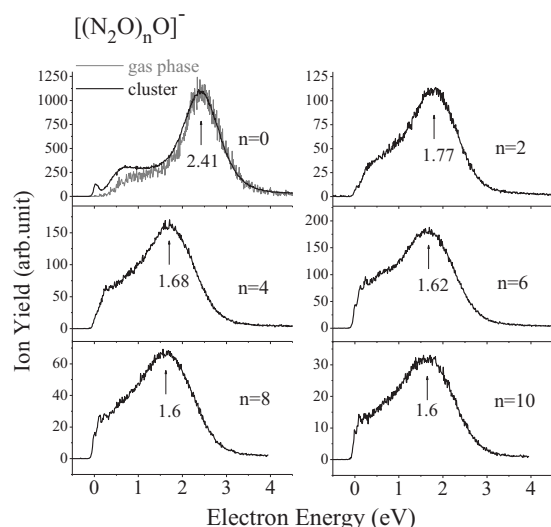

FIG. 2. Formation of complexes of the type $[(N_2O)_nO]^-$ (solvated fragment anions) including O^- (n=0) observed from electron attachment to N_2O clusters (stagnation pressure of 3 bar and nozzle temperature of 220 K).

yields shifts to lower energy with increasing cluster size as already documented in the earlier studies.[19,20] This behavior can be rationalized qualitatively by the solvation shift in the initial transition (generating the target cluster anion) and eventually some additional energy dependence for the decomposition into the particular ion under observation. One can assume that out of the cluster distribution in the molecular beam, larger product ions are formed from larger target clusters, which in turn are subjected to larger solvation shifts for the initial transition. The second observed feature is an increasing relative intensity in the low energy range with increasing size of the observed product ion.

Thus, it appears that in clusters, additional mechanisms for the ion production in the low energy region become operative. This is already visible for the naked fragment ion O^- generated from clusters which exhibits a stronger relative intensity in the range between 0.5 and 1.5 eV and a small peak right at 0 eV (Fig. 2, top, left). This peak is an effect of the cluster environment and not a temperature effect, which is obvious from variation of the nozzle temperature between 220 and 300 K leaving the shape of the O^- ion yield from clusters virtually unaffected (not shown here). As can be seen in Fig. 2, O^- from a free N_2O molecule, on the other hand, does not show a signal at zero energy at room temperature, as also demonstrated by previous high resolution studies.[13,20] The threshold energy for O^- formation via the DEA reaction

$$e^- + N_2O \rightarrow O^- + N_2 \qquad (1)$$

is predicted at 0.26 eV by using both the standard heats of formation for the involved particles (300 K, see Table I) or the $O-N_2$ bond dissociation[5,24,25] energy and electron affinity of O.

The formation of the naked fragment ion O^- from a cluster can be considered to proceed along the reaction

$$e^- + (N_2O)_n \rightarrow O^- + N_2(N_2O)_{n-1}. \qquad (2)$$
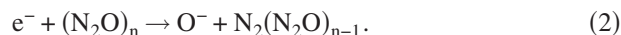
Interestingly, O^- from clusters [reaction (2)] becomes energetically accessible already near 0 eV. In contrast to single N_2O molecules, a cluster carries some quanta of excited intermolecular vibrations even when generated by adiabatic expansion. This amount of internal energy can support DEA at 0 eV. Due to the increasing electron attachment cross section with decreasing electron energy, such *hot band* transitions are well documented in DEA and can be quite pronounced in spite of a low population of vibrationally excited levels.[26] In addition, N_2O is *thermodynamically* unstable with respect to decomposition into $N_2+1/2O_2$. From *energetics,* it is hence possible that electron capture by N_2O clusters generates O_2 and N_2 in addition to O^- formation, thereby gaining energy to drive the reaction at 0 eV. In the case of the trimer, e.g., the reaction

$$e^- + (N_2O)_3 \rightarrow O^- + 3N_2 + O_2 \qquad (3)$$
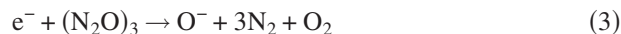
is exothermic by 1.5 eV (see Table I).

The *mechanism* of the reaction near 0 eV is mediated by vibrational Feshbach resonances as already documented by the scattering experiments to single N_2O (Ref. 13) and the ultrahigh resolution laser attachment experiment to N_2O clusters.[21] The incoming low energy electron is trapped in a
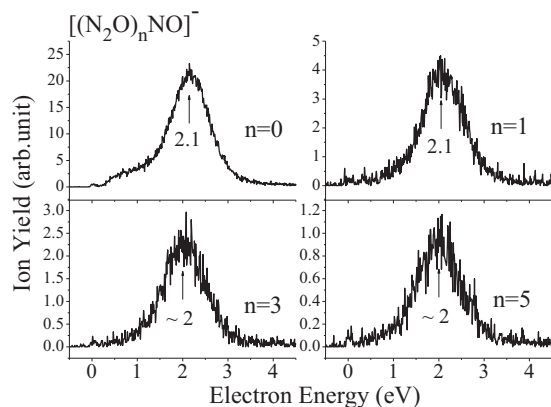
FIG. 3. Formation of complexes of the type $[(N_2O)_nNO]^-$ (solvated fragment anions) including NO^- (n=0) observed from electron electron attachment to N_2O clusters (stagnation pressure of 3 bar and nozzle temperature of 220 K).

diffuse state (formed by weak attractive forces), which couples to the dissociation continuum. It is likely that the O^- ion formed by DEA in the initial step within the cluster triggers an ion-molecule reaction with N_2O possibly generating $NO^- + NO$ like in reaction (4) below.

From Fig. 2, it is apparent that in the ion yields of $[(N_2O)_nO]^-$, (i) the relative intensity at very low energies increases with the size of the complex under observation, and (ii) along the same line, the maximum of the contribution assigned to the shape resonance (in the isolated molecule located at 2.5 eV) is shifted to lower energies and located at 1.6 eV for the complex $[(N_2O)_{10}O]^-$. As already mentioned above, this shift can be explained qualitatively by an increasing solvation energy of the negative charge with increasing size of the target cluster under the reasonable assumption that average larger ionic complexes are formed from larger neutral target clusters. The stronger intensity near threshold indicates that low energy attachment processes, associated with the diffuse negative ion state, play a larger role when the size of the target cluster is increased. A similar effect is observed in a recent study of electron attachment to CO_2 clusters.[23]

A closer inspection of the threshold region reveals that the $[(N_2O)_nO]^-$ and $(N_2O)_n^-$ ion yields carry signatures of vibrational Feshbach resonances which will be considered below.

## B. Formation of the complexes $[(N_2O)_nNO]^-$

These ionic complexes are created within the energy region of the shape resonance and the maximum of the ion yield is located near 2.0 eV, essentially independent of the size of the observed complex, as shown in Fig. 3. Since neither NO^- nor NO is formed from single molecules, the corresponding reactions are considered to be the result of ion-molecule reactions within the target cluster. The formation of NO^- from single molecules, on the other hand, would require an energy of 4.9 eV (see Table I). From clusters, the NO containing complexes are formed at significantly lower energy and the underlying reaction must hence generate products at sufficiently low energy.

The fact that the formation of $[(N_2O)_nNO]^-$ is operative within the energy domain of the shape resonance(s) (generating O^- from single molecules) one can assume that the initial step is the formation of O^- via DEA by an individual molecule within the target cluster. NO^- from N_2O clusters was already reported in the early work by Klots and Compton.[18] They proposed that the origin of NO^- is the reaction

$$e^- + (N_2O)_2 \rightarrow NO^- + N_2 + NO, \tag{4}$$
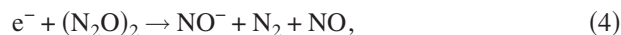
which occurs in two stages. The first is DEA in the dimer according to

$$e^- + (N_2O)_2 \rightarrow (N_2O)O^- + N_2, \tag{4a}$$
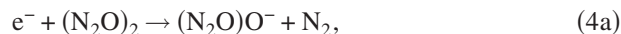
followed by the reaction

$$(N_2O)O^- \rightarrow NO + NO^-. \tag{4b}$$

The ion-molecule reaction between free O^- and free N_2O is known to have an appreciably high rate constant decreasing with the collision energy.[27,28] Since in electron attachment to N_2O, the fragment ion O^- is generated with only small excess energy (0.2 eV) (Ref. 7), we can expect that also within the cluster reaction (4b) is effective.

In the presence of one or more N_2O molecules (i.e., in electron attachment to larger clusters), the products of the ion molecule reaction (4b) can undergo a further reaction, viz.,

$$(NO)(N_2O) \rightarrow N_2 + NO_2, \tag{4c}$$
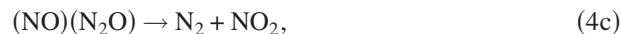
which is exothermic by -1.95 eV.

For the formation of the complexes $[(N_2O)_nNO]^-$, we hence end up with the following two reactions:

$$e^- + (N_2O)_{n+2} \rightarrow [(N_2O)_nNO]^- + N_2 + NO, \tag{5}$$

$$e^- + (N_2O)_{n+3} \rightarrow [(N_2O)_nNO]^- + 2N_2 + NO_2, \tag{6}$$

the minimum cluster size to generate the naked NO^- via reaction (5) would hence be the dimer and via Eq. (6) the trimer. On the basis of the available thermochemical data (see Table I) the exothermicity is obtained as -0.5 eV and -2.0 eV for reaction (5) and (6), respectively, minus the value of the unknown binding energy of the excess electron (electron affinity) in the complexes $[(N_2O)_nNO]^-$. In this estimation it is assumed that the intramolecular binding energy in the neutral (left) and ionic complexes (right) is approximately balanced. Reaction (5) occurs in two steps, the analog to Eqs. (4a) and (4b) and in reaction (6), the ionic complex is additionally subjected to the exothermic reaction (4c) between two neutrals.

From the solvation shift of $(N_2O)_nO^-$, representing the first step (4a) of the proposed reaction generating $[(N_2O)_nNO]^-$, one would expect that also the peak maximum of $[(N_2O)_nNO]^-$ would be shifted to lower electron energy with increasing n. Hence, the question remains open why this peak position is essentially independent of the cluster size (Fig. 3). One possible explanation could be that a small energy barrier (activation energy) has to be overcome for reaction (4b) to occur.

On the basis of the electron affinity of the single isolated compounds NO (0.03 eV) and N_2O (0.22 eV), it is likely that
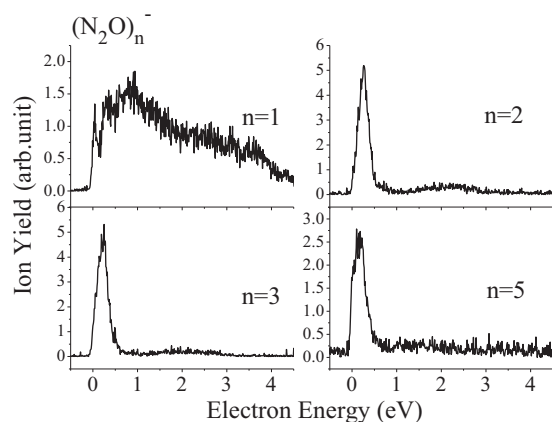
FIG. 4. Formation of nondecomposed complexes of the type $(N_2O)_n^-$ including the monomer N_2O^- (n=0) observed from electron electron attachment to N_2O clusters (stagnation pressure of 3 bar and nozzle temperature of 220 K).

in the complexes $[(N_2O)_nNO]^-$, the excess charge is localized rather on the $(N_2O)_n$ entity than on NO, except in the case of naked NO^-, representing the lowest member of the homologous series $[(N_2O)_nNO]^-$ (n=0).

The formation of the complexes $[(N_2O)_nNO]^-$ is an impressive example which demonstrates that in molecular clusters reactions can be triggered by low energy electron attachment involving multiple bond rupture and formation of new bonds. The necessary energy is provided by the formation of stable ionic and neutral products like O^-, N_2 and O_2, and NO_2 [reactions (3)–(6)].

C. Formation of the nondecomposed cluster ions $(N_2O)_n^-$ and observation of VFRs in ion yields

The nondecomposed cluster ions including the monomer are preferentially observed at very low energy and only a small contribution is visible in the energy domain of the shape resonance(s), as can already be seen in Fig. 1. Figure 4 shows a few members of the series $(N_2O)_n^-$ indicating that in the threshold region reproducible sharp structures appear. These structures are more pronounced at particular expansion conditions (see Fig. 5) and are assigned to VFRs, as also
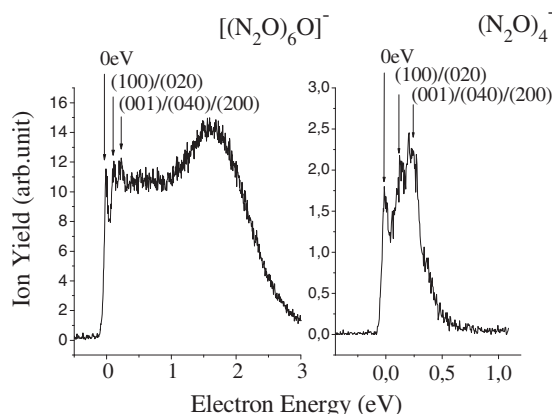

FIG. 5. Ion yields of $[(N_2O)_6O]^-$ and $(N_2O)_4^-$ in the threshold region recorded at a stagnation pressure of 4 bar and a nozzle temperature of 300 K. The sharp structures are due to VFRs (see the text).

previously observed in the ultrahigh resolution electron attachment studies to N_2O clusters[21] and also in the O^- yield for DEA to free N_2O molecules.[13]

The formation of nondecomposed anions in clusters is usually described by stabilization of the transient negative ion (TNI) via intramolecular collisions formed in the initial attachment step.[29] The TNI in the cluster is principally subjected to a competition between DEA (forming either a naked fragment ion (in the present case O^-) or solvated fragment ions $[(N_2O)_nO]^-$) and stabilization by intramolecular collision, forming the nondecomposed ionic complexes $(N_2O)_n^-$.[29] Apparently, within the shape resonance region around 2 eV, DEA strongly prevails generating $[(N_2O)_nO]^-$ (n≥0) and only little intensity of nondecomposed ionic complexes is observed. This can be rationalized by the decomposition mechanism in the electron energy range between 1 and 3 eV, which is repulsive as obvious from the doublet in the TOF spectrum.[7] This apparently favors the formation of the solvated ions $[(N_2O)_nO]^-$ over stabilization. Electron attachment below 1 eV, on the other hand, initially generates molecular anions with no particular repulsive character and they consequently tend to generate the relaxed, nondecomposed complexes $(N_2O)_n^-$.

The ion yield for the monomer N_2O^- differs substantially from those of the higher members of the homologous series. It should be noted that the monomer anion is not observed in electron attachment to N_2O under single collision conditions since effective mechanisms for stabilization of the TNI are not operative. The different shape in the ion yield is an indication that in the energy range above 0.4 eV, the precursors of N_2O^- are possibly complexes of the type $[(N_2O)_nO]^-$ subjected to (endothermic) electron transfer.

Figure 5 finally presents the ion yields of $[(N_2O)_6O]^-$ and $(N_2O)_4^-$ in the threshold region showing the presence of sharp structures assigned as VFRs. These spectra were obtained at a nozzle temperature of 300 K and at a stagnation pressure of 4 bar resulting in significantly more pronounced structures than under the expansion conditions of Figs. 2 and 4 (220 K/3 bar). The average size of the target cluster is quite similar between the two expansion conditions and one might expect that the dominant effect is due to the higher temperature. The energies of the normal vibrations in N_2O are 159.3 (ν_1, symmetric stretch), 73.0 (ν_2, bend), and 275.7 meV (ν_3, asymmetric stretch).[30] Although the electron energy resolution is not sufficient to distinguish between two quanta of the bending and one quantum of the symmetric stretch or one quantum of the asymmetric stretch and 4 quanta of the bonding mode vibration, it is obvious that all three normal modes are actively involved in the VFRs.

IV. CONCLUSION

Electron attachment to N_2O clusters leads to the production of $[(N_2O)_nO]^-$, $[(N_2O)_nNO]^-$, and $(N_2O)_n$ anions, the first being the predominant fragment. At a very low energy, vibrational Feshbach resonances are observed for both $(N_2O)_n^-$ and $[(N_2O)_nO]^-$. The narrow peaks attributed to vibrational excitation become much more distinguishable for larger clusters and for measurements performed with the

nozzle at room temperature. A second resonance is observed at around 2 eV for $[(N_2O)_nNO]^-$ and $[(N_2O)_nO]^-$ and very weakly for $(N_2O)_n^-$. In this energy range, the formation of $[(N_2O)_nNO]^-$ by DEA is not thermodynamically possible, the observed fragments are likely to be originating from $[(N_2O)_{n+1\ or\ 2}O]^-$ followed by internal ion-molecule reaction(s).

AKNOWLEDGMENTS

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