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Electron attachment to nitric oxide clusters and electron impact ionization of carbon monoxide clusters

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Abstract. The formation of both positively and negatively charged ions after interaction of electrons with different cluster beams is investigated, by the use of highly monochomatized electron beams. In the case of the electron attachment to neutral NO clusters, the formation of the monomer ion NO^- could be observed for the first time. The only explanation for the creation of such an ion is an intracluster reaction. In the case of carbon monoxide clusters, the appearance energies were determined with high accuracy. From these data, we derived the binding energy of the cluster dimer. Our results are in good agreement with photoionization studies.

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1 Introduction

Electron attachment studies are of fundamental importance to the understanding of electron molecule and electron cluster interaction and the mechanisms of negative ion formation. Electron impact ionization is an important tool in the study of molecules and clusters: in particular, that concerning the production and identification of the corresponding ions in mass spectrometry and related studies. For both electron attachment and electron impact ionization, electron beams with a good electron energy resolution and an accurate calibration of the energy scale are necessary. With our hemispherical and trochoidal electron monochromators developed recently we are able to measure appearance energies of clusters and molecules with a high accuracy comparable to that of photoionization techniques using synchrotron radiation.

2 Experimental

The electron attachment measurements were carried out through a crossed-beam experiment using a trochoidal electron monochromator (TEM) as an electron beam source. The best energy resolution achieved is about 5 meV (full widths at half maximum) and electron energies close to zero are possible. Using a combination of either a temperature-controlled effusive molecular beam source or a supersonic nozzle source and a quadrupole mass spectrometer for analysis of the anions produced, one can measure both electron attachment spectra as a function of electron energy and target beam properties such as gas temperature and target composition. The energy resolution and the zero-energy position of the energy scale were calibrated and checked with the known cross-section curve for Cl^- from CCl_4 [1, 2]. The appearance energies of carbon monoxide cluster ions were measured with a hemispherical electron monochromator (HEM) with a best electron energy resolution of about 50 meV and an upper estimation for the energy scale accuracy of 10 meV.

3 Results and discussion

3.1 Electron attachment to nitric oxide clusters

Recently, electron attachment to O_2 clusters was investigated in detail, and on top of a typical s-wave attachment cross section, a fine structure due to the vibrational modes of the anion were found. The identification of the vibrational levels that are involved in the attachment process is possible because of the different spacings between the vibrational levels. The vibrational spacings observed could be quantitatively accounted for by model calculations [3]. The system NO is similar to O_2 in that the extra electron occupies an antibonding molecular orbital (MO); this results in a larger equilibrium geometry of the anion. However, the adiabatic electron affinity of NO is only 26 ± 5 meV [4] and is thus considerably smaller than that of O_2. In contrast to O_2, NO has a dipole moment

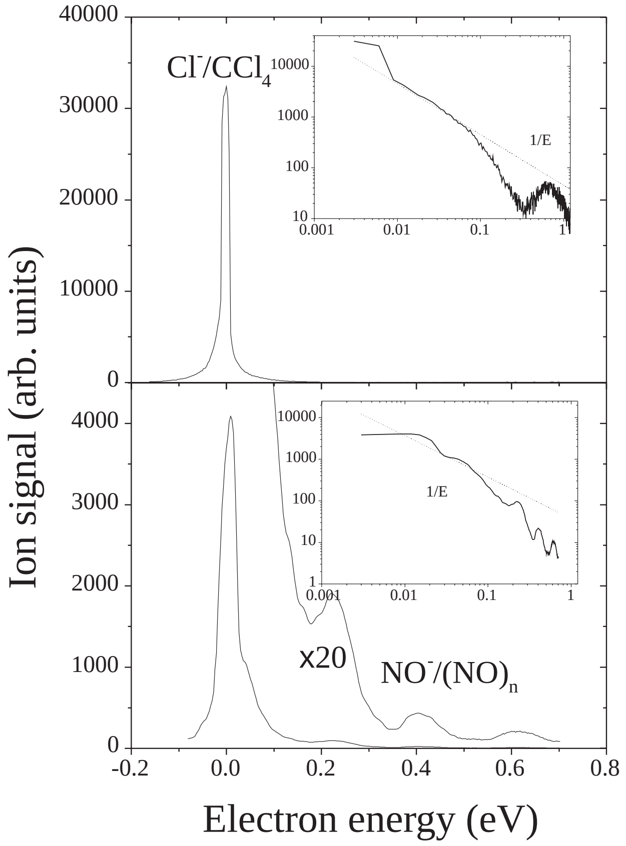

Fig. 1. Measured NO^- signal observed from electron attachment to an NO cluster beam as a function of the electron energy. In the upper figure, Cl^-/CCl_4 is shown as reference.

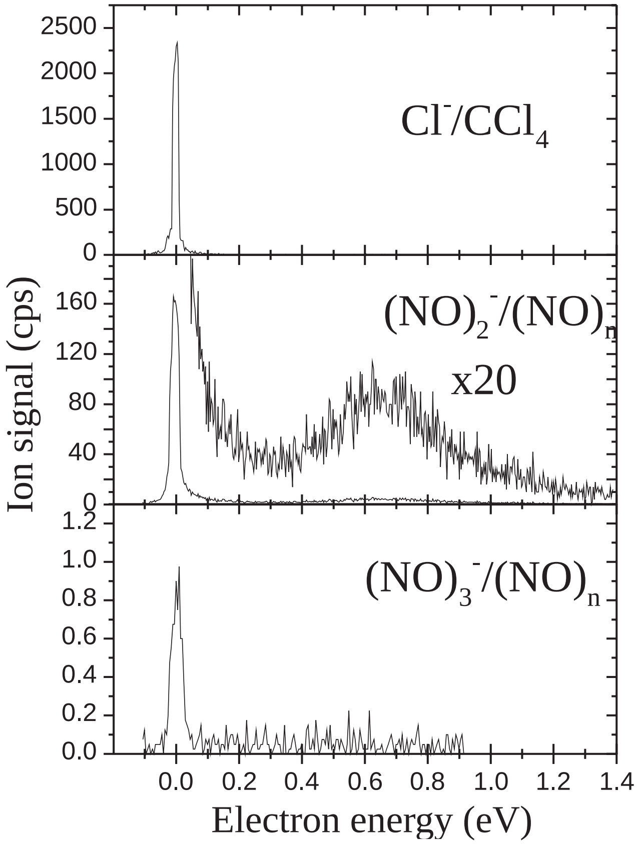

Fig. 2. $N_2O_2^-$ and $N_3O_3^-$ signals from electron attachment to NO clusters, as a function of the electron energy. The energy calibration signal Cl^- from CCl_4 is also shown, indicating the energy resolution.

(0.16 D) [5], so that an appreciable contribution of direct inelastic scattering may contribute to vibrational excitation of neutral NO. Also, vibrationally excited NO^- has a much shorter autodetachment lifetime as compared to the O_2^-; this may also affect the electron attachment behavior in clusters [6, 7]. The relative attachment cross section for NO^- formation (for more details see [7]) shows a very sharp peak close to zero eV and a series of further weak peaks (see Fig. 1). While the attachment mechanism is probably similar in both systems, the evolution of the ionized cluster system must be different in the case of NO. The zero-energy peak is interpreted as *s*-wave capture ($\sigma \propto E^{-1}$). The positions of the other peaks are located on the basis of a series of experiments at 40 ± 10 meV, 220 ± 10 meV, and 410 ± 10 meV, corresponding to a spacing of 180 ± 20 meV and 190 ± 20 meV. The vibrational frequency of NO^- is given from 166 ± 10 meV [8] to 180 ± 25 meV [9]. The most recent value is obtained from an autodetachment study in NO^- [10] as 159 ± 1 meV. In contrast, for neutral NO the vibrational frequency of 236 meV [11] is considerably larger. From these numbers, it is clear that the observed structures cannot directly be correlated to vibrational excitation of neutral NO, although the direct scattering mechanism for vibrational excitation may be operative in the present system. While the vibrational frequency of neutral NO is well established, the numbers given above indicate that this may not be true for NO^-. The vibrational frequency of a molecule bound in a cluster may be perturbed, in particular in the presence of appreciable coupling, as in the case of a molecular ion like NO^-. So we tentatively assign the observed structures as transitions to vibrationally excited solvated NO^-. Due to the very low adiabatic electron affinity of NO and the strong anion dimer bond,

$$(NO)_n + e^- \longrightarrow NO^- + \text{neutral products} \qquad (1)$$

cannot be the result of an evaporative attachment reaction, i.e., evaporation of monomer units until the single ion is left. Evaporative attachment via

$$(NO)_n + e^- \longrightarrow NO^- + (n-1)NO \qquad (2)$$

would require the energy equivalent of $(n-1)$ monomer dissociation energies minus the electron affinity of NO. The binding energy for the NO dimer is known from high-resolution photodetachment experiments [12] as $D(NO\text{–}NO) = 98$ meV. Since the experiments with NO are carried out under similar expansion conditions, as in the case of oxygen, and since the intermolecular forces are larger in NO, we assume that the neutral clusters contain on average

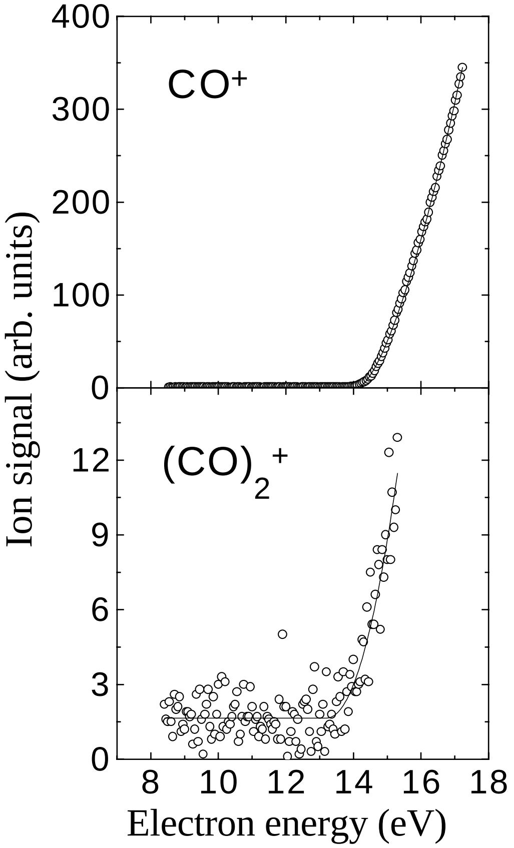

Fig. 3. Ionization efficiency curves for the production of CO^+ and $(CO)_2^+$ by electron impact ionization of a neutral CO cluster beam.

more than 20 molecules. In any case, even for the dimer, or under the most unprobable assumption that NO^- leaves a completely undissociated neutral cluster when formed, reaction (2) will remain endothermic, since the bond dissociation energy $D[(NO)_m - NO^-]$ is in any case considerably larger than the electron affinity of NO. A possible solution to this problem is the formation of neutrals in the course of reaction (1), which are more stable than their neutral NO counterparts, and thereby would provide the necessary energy. Possible reactions are

$$(NO)_n + e^- \longrightarrow NO^- + N_2 + O_2 + (n-3)NO \qquad (3)$$
$$\longrightarrow NO^- + N_2O + NO_2 + (n-4)NO \qquad (4)$$

which are highly exothermic. It is known that the weakly bound complex $NO^- \cdot NO$ correlates (probably without barrier) to an $[ONNO]^-$ ion, which is about 2 eV below the $NO^- \cdot NO$ system. This $[ONNO]^-$ ion itself is separated by an activation barrier from another isomer $[NNO_2]^-$ of comparable stability. Such ionic intermediates could be considered to be acting as catalysts for a reaction generating N_2 and O_2 from the $e^-/(NO)_n$ system. This is certainly a highly speculative explanation, upon which one may immediately ask why O_2^- and NO_2^- are not detected. From Fig. 2, it can be seen that ions of the composition $N_2O_2^-$ and $N_3O_3^-$ are, in fact, formed in the present experiment.

3.2 Electron impact ionization of carbon monoxide clusters

For electron impact ionization of atoms and small molecules, the ionization efficiencies rise in the vicinity of the threshold E_0, with the excess energy rising to the power of the corresponding charge state (zth power law). In the case of large molecules, especially clusters, many different ionic states can be reached by electron impact ionization, and therefore the onset region of the ionization efficiency curve consists of the sum of many individual cross sections (one for each electronic state). That is why the threshold region is curved more strongly than predicted by the zth power law, and why it is difficult to extract appearance energies from the experimental data. With a recently developed method [13] and using a HEM monochromator [14], we are able to determine appearance energies with an average deviation of about ±10 meV. Applying our new data analysis procedure [13] to the monomer, dimer, and trimer ions produced by electron impact ionization of a $(CO)_n$ cluster beam, we obtain, after calibrating the energy scale to the known CO monomer ionization energy of 14.0142 ± 0.0003 eV [15], the following appearance energies: $AE((CO)_2^+) = 13.194 \pm 0.10$ eV and $AE((CO)_3^+) = 12.98 \pm 0.34$ eV. The errors given are statistical, and include the errors from the fit to the monomer and cluster signals. The present values are in fair agreement with previous high-resolution VUV photoionization experiments [16] reporting values of 13.05 ± 0.04 eV and 12.91 ± 0.04 eV. Using the present ionization energies, the known ionization energy of CO, and the estimated dissociation energy for $(CO)_2$ and $(CO)_3$, the bond energies for $CO^+ - CO$ and $(CO)_2^+ - CO$ are calculated to be 0.83 ± 0.10 eV and 0.22 eV, respectively. The corresponding values derived in the photoionization study are 0.97 ± 0.04 eV and 0.16 ± 0.08 eV, respectively. It is interesting to note that there exist a number of further experimental results on $AE((CO)_2^+)$ as summarized by Weitzel and co-workers [17] ranging from 13.15 eV down to 12.73 eV. Moreover binding energies have been reported to be as high as 1.96 eV (see [17]). Thus the difference between experimental values ranging from 0.8 eV to 1.96 eV (with a recent value of 1.80 eV [17]) and a theoretical value of 2.68 eV [18] is quite puzzling and we are presently therefore reexamining this question with an improved experimental set-up.

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