



Mean excitation energies for molecular ions



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ABSTRACT

The essential material constant that determines the bulk of the stopping power of high energy projectiles, the mean excitation energy, is calculated for a range of smaller molecular ions using the RPA method. It is demonstrated that the mean excitation energy of both molecules and atoms increase with ionic charge. However, while the mean excitation energies of atoms also increase with atomic number, the opposite is the case for mean excitation energies for molecules and molecular ions. The origin of these effects is explained by considering the spectral representation of the excited state contributing to the mean excitation energy.

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1. Introduction

The deposition of energy by a fast hadronic ion into a gaseous target made up of a variety of components including atoms, molecules, and ionic versions of both, is of central importance for the understanding of many fundamental processes in physics. Systems of this sort include, but are not restricted to, reactor plasmas [1,2], liquid crystals [3], planetary atmospheres [4], and intergalactic space [5]. In all of these systems, although they have widely different densities (n), the incoming projectile deposits energy into the mixture of atoms, molecules, ions of both the foregoing, and electrons. The understanding of such energy deposition relies on knowledge of the fundamental electronic properties of the constituents' material particles.

The quantity most important in the description of energy deposition by ions in materials is the stopping power of the target material, which is the loss of kinetic energy of a projectile with velocity v per unit path length in the target: $-dE(v)/dx$. The kinetic energy absorbed from the projectile is converted to target electronic energy, and thus depends on the electronic structure of the target. The stopping power of a material depends on the material density, n , and is thus frequently normalized to target particle density, and is referred to as the stopping cross section, $S(v)$, of the material.

$$S(v) = -\frac{1}{n} \frac{dE(v)}{dx} \quad (1)$$

In the simplest case, that of Bethe stopping [6], the stopping cross section of each component i of the target can be written:

$$S_i(v) = \frac{4\pi e^2 Z_1^2 Z_{2,i}}{m v^2} L_i(v) \quad (2)$$

Here Z_1 and $Z_{2,i}$ are the projectile charge and target electron number, respectively, and $L_i(v)$ is known as the stopping number of component i (here and in the following, super- or subscript indicates the component i , not a power). The stopping number of each component can then be written:

$$L_i(v) = \ln \frac{2m v^2}{I_0^i} - \frac{C(v)_i}{Z_{2,i}} \quad (3)$$

The second term in Eq. (3) is known as the shell corrections, and corrects for the fact that the velocity of the projectile may not be much larger than that of the target electrons, especially for inner shell electrons. That the projectile velocity is much larger than that of the target electrons is one of the basic assumptions of simple Bethe theory [6].

The mean excitation energy of each component i , I_0^i , measures the ability of each component of the target to absorb energy from the projectile. At this level of approximation, this is the first energy weighted moment of the dipole oscillator strength (f) distribution (DOSD) for each component of the target [6]:

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Table 1
Spin Multiplicity, Mean Excitation Energy in the Dipole Length Approximation (I_0^L), and TRK Sums in the Dipole Length (S_L) and Dipole Velocity (S_V) Approximation of Polyatomic Anions and Neutrals calculated with the aug-cc-pCV5Z basis set.

	Spin	I_0^L (eV)	S_L	S_V	
C ₂	1	69.83	12.00	11.99	a, b
C ₂ ⁻	2	56.94	13.01	13.00	b
CN	2	76.30	13.00	13.00	
CN ¹⁻	1	64.44	14.00	14.00	a
OH	2	82.37	9.00	9.00	b
OH ¹⁻	1	64.97	10.08	9.94	

a: detected in the interstellar medium.

b: calculated as ROHF or MCSCF with DALTON.

Table 2
Spin Multiplicity, Mean Excitation Energy in the Dipole Length Approximation (I_0^L), and TRK Sums in the Dipole Length (S_L) and Dipole Velocity (S_V) Approximation of Polyatomic Cations and Neutrals calculated with the aug-cc-pCV5Z basis set.

	Spin	I_0^L (eV)	S_L	S_V	
H ₃	2	16.49	3.00	3.00	
H ₃ ⁺	1	20.88	2.00	2.00	a
CH	2	56.14	7.00	6.99	a,b
CH ¹⁺	1	71.80	6.00	6.00	a
CH ₂	3	50.86	8.00	8.00	a
CH ₂ ¹⁺	2	62.74	7.00	7.00	
CH ₂ ²⁺	1	75.28	6.00	6.00	
CH ₃	2	46.64	9.00	9.00	
CH ₃ ⁺	1	55.85	8.00	8.00	
CH ₃ ²⁺	2	60.50	7.00	7.00	
CH ₄	1	43.47	10.00	10.00	a
CH ₄ ⁺	2	48.92	9.00	9.00	
CH ₄ ²⁺	1	54.11	8.00	8.00	
NH	3	69.17	8.00	8.00	
NH ¹⁺	2	76.51	7.00	7.00	b
NH ₂	2	60.79	9.00	9.00	
NH ₂ ⁺	3	74.11	8.00	8.00	b
NH ₂ ²⁺	2	86.02	7.00	7.00	b
NH ₃	1	54.91	10.00	10.00	
NH ₃ ⁺	2	65.59	9.00	9.00	
NH ₃ ²⁺	1	74.18	8.00	8.00	
OH	2	82.37	9.00	9.00	b
OH ¹⁺	3	100.17	8.00	8.00	

a: detected in the interstellar medium.

b: calculated as ROHF or MCSCF with DALTON.

$$\ln I_0 = \frac{\int \frac{df}{dE} \ln E dE}{\int \frac{df}{dE} dE} \quad (4)$$

The stopping power of a target which is composed of a mixture of non-interacting components is then given, according to the Bragg Rule [7], by the density weighted sum of the stopping powers of the target components:

$$\left(-\frac{dE}{dx} \right)_{\text{target}} = \sum_{\text{components}} n_i \left(-\frac{dE}{dx} \right)_i \quad (5)$$

Thus the stopping power of the target containing a mixture of components, where $n = \sum_{\text{components}} n_i$ is:

$$\left(-\frac{dE}{dx} \right)_{\text{target}} = \frac{4\pi e^2 Z_1^2}{m v^2} \sum_i n_i Z_{2,i} \ln \frac{2m v^2}{I_0^i} \quad (6)$$

Consequently, in order to know the magnitude of the energy deposition of a fast ion in a target, the mean excitation energy, and thus the stopping cross section, of each of the target components must be determined.

The stopping power of the electron gas is well known [8], as is that for many atoms [9] and even some atomic ions [10]. There are also many determinations of the mean excitation energies of small

molecules in the literature [11], but not for molecular (polyatomic) ions. Since such ions exist in many systems, as mentioned above, it is necessary to have mean excitation energies for such ions to understand the processes involved.

In the present work, we report calculations of the mean excitation energies of several small molecular ions, some of which have been detected in the interstellar medium. These cases are noted in the tables by (a).

2. Computational details

Calculations were carried out on several small polyatomic molecules, ions and their constituent atoms. The minimum energy geometry for the target ions was first determined using the coupled cluster program CFOUR [12] at the CCSD(T) level, and using the cc-pVTZ basis, a level of correlation and basis set choice known to give reliable geometries, as e.g. shown in a very recent benchmark study for 122 molecules [13]. The dipole oscillator strengths, in the length and velocity representations were then calculated at the level of time-dependent Hartree-Fock theory also known, as the random phase approximation (RPA), using the TURBOMOLE program [14,15]. In the case of the open shell systems, the calculations were carried out using the Unrestricted Hartree-Fock (UHF) method. For a few systems, due to instability problems in the UHF calculations in TURBOMOLE, the calculations were carried out with the Restricted Open Shell Hartree-Fock (ROHF) or Multi-configurational self-consistent field (MCSCF) methods using the DALTON program [16]. These cases are marked with “b” in Tables 1 and 2 below. In all cases, the aug-cc-pCV5Z basis was used for C, N, O, and F, and the aug-cc-pV5Z for H as in our previous work on the atomic ions [10]. Recently, we have found [17] that inclusion of electronic correlation beyond RPA has little effect on mean excitation energies. However, the same study also shows that rather large augmented, correlation consistent basis sets of the kind used in this study are needed in order to obtain a reliable representation of all the excited states in a sum-over-states calculation of I_0 . It should be noted that the Random-Phase Approximation includes all electron correlation through first order in the fluctuation potential for both the ground and excited states and that it thus calculates the excitation energies and transition moments consistently through first order [18,19].

According to the Thomas-Reiche-Kuhn (TRK) sum rule [20], the dipole oscillator strengths for a system should sum to the number of electrons in the system,

$$\sum_n f_{n0} = N \quad (7)$$

which should be valid for the length, velocity, and mixed forms of the oscillator strength. For anions with a charge -2 or larger, the TRK sum rule was in general found not to be fulfilled with this basis set, and thus the mean excitation energies for these cases are not reported.

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