Metastable C_2^{2-} Dianion

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A metastable molecular dianion C_2^{2-} in a closed-shell ${}^1\Sigma_g^+$ state has been found. Using a complex absorbing potential in conjunction with a multireference configuration interaction wave function, the resonance position and width are calculated and their dependence on the nuclear charge Z is examined. Based on our findings the interpretation of a recent scattering experiment is questioned and an alternative experiment is proposed. [S0031-9007(97)03848-9]

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Dianionic species as small as O^{2-} or SO_4^{2-} are very common in solid state and solution chemistry, but it has only recently been shown that small doubly negative charged systems may exist as isolated entities [1,2]. In fact the smallest dianions which have been observed in a mass spectrometer (implying lifetimes of at least 10^{-5} sec) are C_7^{2-} [3] and $S_2O_6^{2-}$ [4]. Based on *ab initio* calculations many smaller systems have been predicted to form long-lived dianions [1], which consist typically of a central metal atom and three to eight fluorine or chlorine ligands. The smallest dianion predicted to be long-lived is LiF_3^{2-} [5].

However, even if small solid-state dianions are unstable in the gas phase, they may nevertheless exist as short-lived metastable species. It is not possible to detect such *temporary* dianions directly in a mass spectrometer, but one may observe them as resonance structures in electron scattering from the associated monoanion. Reports on electron scattering from monoanions, especially in the energy region of only a few eV are rare, but recently the electron impact detachment cross section of the three anions H^-, O^-, and C_2^- has been measured [6–9]. Both the detachment cross sections of H^- and O^- are smooth functions of energy and show no resonance structure. In contrast, in scattering from C_2^- the detachment cross section exhibits a broad feature at an energy of about 10 eV, which has been interpreted in terms of a closed-shell C_2^{2-} resonance state [9].

From a theoretical point of view the treatment of a resonance state is far more involved than the description of bound states and so far only calculations on metastable states of atomic dianions have been reported [10,11]. In this Letter we present evidence for a resonance state of C_2^{2-} which is to our best knowledge the first theoretical examination of a metastable molecular dianion in the literature. Specifically we investigate the closed-shell ${}^1\Sigma_g^+$ state of C_2^{2-} which is isoelectronic with the neutral N_2 molecule exhibiting the electron configuration

$$(\text{core})^4(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^4(2\sigma_g)^2.$$

We emphasize that a metastable closed-shell state cannot be classified by one of the schemes developed for *monoanionic* resonances [12], since all monoanions possessing rare-gas-like electronic structures are bound.

We begin with a brief description of the C_2^- and C_2 states relevant in the present context. It is a well known fact that the target anion C_2^- possesses three bound electronic states [13–15]. The electronic ground state shows ${}^2\Sigma_g^+$ symmetry and at roughly 0.6 and 2.4 eV above it there are excited states of ${}^2\Pi_u$ and ${}^2\Sigma_u^+$ symmetry, respectively. These three states may be represented by electron configurations exhibiting one hole in the $2\sigma_g$, the $1\pi_u$, and the $1\sigma_u$ orbitals, respectively. The neutral C_2 molecule exhibits a ${}^1\Sigma_g^+$ ground state which is about 3.4 eV above the ${}^2\Sigma_g^+$ ground state of C_2^-, and possesses several other low lying states [13]. Thus, depending on the resonance position of the metastable C_2^{2-} state there may be up to three open one-electron and various open two-electron detachment channels.

A first approximation for the resonance position can be obtained by an extrapolation where the nuclear charge Z is treated as a parameter [16,17]. To this end Z is increased such that the state of interest becomes bound and for a number of different Z values the energies of the relevant states are calculated employing standard bound state techniques. We have performed high level *ab initio* calculations for the ${}^1\Sigma_g^+$ 10-valence electron (VE), the three 9-VE ${}^2\Sigma_g^+$, ${}^2\Pi_u$, and ${}^2\Sigma_u^+$ states, as well as for the ${}^1\Sigma_g^+$ 8-VE state, where the nuclear distance has been fixed to the bond length of the C_2^- ground state ($R = 1.265$ Å). For details, see [18].

The corresponding results are shown in Fig. 1. As may be expected, the energy differences of the three 9-VE states are almost independent of Z. In contrast, the 10-VE ${}^1\Sigma_g^+$ state is only for $Z \geq 6.3$ stable with respect to electron loss. For smaller Z it becomes instable and moves into the continua of the 9-VE states. Extrapolation of its energy to $Z = 6$ yields a resonance position of roughly 4 eV and an open two-electron escape channel. Comparison of our calculated energy differences with the

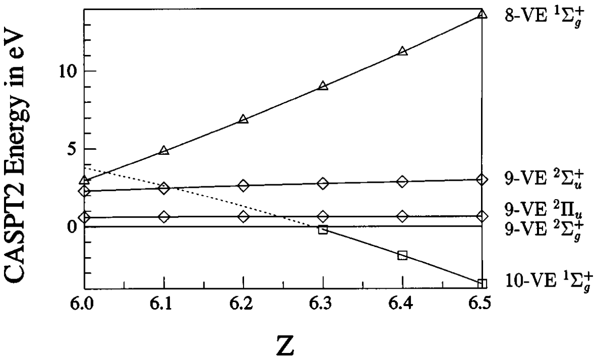

FIG. 1. The energies of the 8-VE, 9-VE, and 10-VE states discussed in the text are shown relative to the 9-VE $^2\Sigma_g^+$ ground state. The data have been obtained at a highly correlated level of theory [18] and the energy of the 10-VE $^1\Sigma_g^+$ has been extrapolated to $Z < 6.3$.

experimentally known electron detachment energies of the three C_2^- states ($Z = 6$) and the ionization potentials of N_2 ($Z = 7$) shows that in our computations the energy differences between states possessing the same number of electrons are accurately reproduced, but energy differences between states exhibiting different numbers of electrons are underestimated by about 0.5 eV. Thus, based on the Z-extrapolation scheme, we expect the resonance position of the C_2^{2-} state to lie definitely below 4 eV and probably close to the energy of the neutral C_2 $^1\Sigma_g^+$ state (3.4 eV).

To obtain reliable values for the energy *and lifetime* of a metastable state in general one has to solve a scattering problem. However, the computation of scattering wave functions is a difficult task, since their non-L^2 nature prevents the application of basis set methods. This has encouraged the development of methods, where the resonance is not extracted from the cross section, but is described by an eigenfunction to a complex Siegert eigenenergy [19,20]

$$E_{\text{res}} = E_R - i\Gamma/2\,, \tag{1}$$

where E_R is the position and $1/\Gamma$ is the lifetime of the resonance. The Siegert energies are obtained directly using complex symmetric Hamiltonian techniques, where the most prominent one is the complex coordinate method [21–23]. We have employed a complex absorbing potential (CAP) which is similar in spirit and allows the use of a *real* L^2 basis set. In the CAP approach [24] an artificial CAP $-i\eta W$, which absorbs the detached electron, is added to the given Hamiltonian H of the system. The resulting effective Hamiltonian

$$H(\eta) = H - i\eta W \tag{2}$$

is complex symmetric, i.e., non-Hermitian, the parameter η denotes the CAP strength, and W is a positive potential function such as r^β [24,25]. The resonance eigenvalue is extracted from the spectrum of $H(\eta)$ using either a stabilization procedure (with respect to η) or by analyzing the corresponding eigenvectors.

We have implemented the CAP method on the multireference configuration interaction (MR-CI) level, where the resonance wave function is described by a set of reference configurations and all single and double excitation with respect to this reference space. The reference space consists of all possible configurations representing one of the three bound C_2^- states plus an extra electron, such that the balance between the C_2^{2-} and the $C_2^- + e$ aspects in the wave function is guaranteed. The real part of the effective Hamiltonian matrix $\mathbf{H}(\eta)$ has been computed employing the MR-CI program developed at the University of Bonn [26], and a block-Lanczos algorithm adapted to the case of complex-symmetric matrices [27] is used to calculate the complex eigenvalues.

Since both the one-particle basis set [18] and the reference space are very large, the dimension of the effective Hamiltonian matrix $\mathbf{H}(\eta)$ has been reduced using one of the following approximations. On the one hand, the MR-CI program offers an energy selection procedure, where the "importance" of a given configuration is estimated using first order perturbation theory, and only configurations more "important" than a given threshold t are retained (see, e.g., [16]). On the other hand, the one-particle basis has been partitioned into a compact part essential for the correlation and a diffuse part needed to describe the absorption of the detached electron. Only those configurations where at most one electron occupies the diffuse part were retained. More technical details will be given in a forthcoming publication [28].

Our findings obtained using either the energy selection procedure or the partitioned one-particle basis are displayed in Table I. Employing the partitioning scheme, we observe that if the size of the compact part is enlarged from 21 to 25 and 30 orbitals the resonance position and width of 2.81 and 0.26 eV are increased by less than 0.1 eV. Making use of the energy selection procedure

TABLE I. Resonance parameters of the $^1\Sigma_g^+$ C_2^{2-} state at different correlated levels of theory. The upper part shows values obtained with a partitioned one-particle basis set, where the compact part consisted of n orbitals. In the lower part the energy selection procedure has been used, where the threshold t is given in m hartree.

	E_{res} (a.u.)	E_R (eV)	Γ (eV)
	Partitioned one-particle basis set		
$n = 21$	$-75.7032 - 0.0048i$	2.81	0.26
$n = 25$	$-75.7116 - 0.0059i$	2.85	0.32
$n = 30$	$-75.7150 - 0.0063i$	2.92	0.34
	Energy selected configuration space		
$t = 0.5$	$-75.7063 - 0.0100i$	3.25	0.54
$t = 0.25$	$-75.7091 - 0.0100i$	3.19	0.54
$t = 0.125$	$-75.7107 - 0.0101i$	3.15	0.55

a constant width of 0.54 eV is obtained; the resonance position, however, is slightly decreased for smaller values of the selection threshold. Analogous trends have been observed for the N_2^- $^2\Pi_g$ shape resonance [28,29] and have been rationalized in terms of a balance between the N_2^- and $N_2 + e$ aspects in the resonance wave function. Based on our numerical results and on the experience with the N_2^- $^2\Pi_g$ shape resonance, we predict the existence of a closed-shell $^1\Sigma_g^+$ C_2^{2-} resonance state at about 3 eV above the $^2\Sigma_g^+$ ground state of the C_2^- anion with a resonance width of about 0.5 eV.

Moreover, we have calculated the Z dependence of the resonance parameters. In the range $6.0 \leq Z \leq 6.15$ the $E_R(Z)$ values lie on a nearly straight line and $\Gamma(Z)$ is shown in Fig. 2. Both curves are smooth and match the trends established with the Z–extrapolation scheme for the bound state energies, i.e., E_R and Γ tend to zero close to $Z = 6.3$. Thus, using the CAP method it is possible to describe the transition of a bound state into a resonance.

It is extremely difficult to compute accurate resonance parameters, but we are sure that our results have the correct order of magnitude. Regarding the many-particle basis sets, our experience with other metastable states and the results in Table I show that the errors introduced by the energy selection as well as by the partitioning scheme are at most of the order of a few tenths of an eV. A shift of similar magnitude might be expected, if the one-particle basis set is extended with more polarization functions of higher angular momentum, but this extension will stabilize the resonance state. Thus, we predict the lifetime of the C_2^{2-} dianion to be about as long as that of the famous N_2^- $^2\Pi_g$ shape resonance. Moreover, we conclude the 10 eV feature in the electron impact detachment cross section [9] cannot be interpreted as a C_2^{2-} state exhibiting an electronic structure analog to the N_2 ground state and should be reinvestigated.

The picture emerging from our calculations is displayed schematically in Fig. 3. The binding energies of the C_2 molecule and the three C_2^- states as well as the electron affinity of the carbon atom have been taken from the literature [14,15,30]. Regarding the metastable C_2^{2-} potential energy curve, a preliminary study of the R dependence of the resonance parameters suggests that the equilibrium bond length of the C_2^{2-} dianion is very close to that of the $^2\Sigma_g^+$ C_2^- state and that both the resonance position and width are fairly stable over a range of 1 Å. Thus, in Fig. 3 we have placed the C_2^{2-} resonance state 3 eV above the C_2^- $^2\Sigma_g^+$ state and its dissociation limit corresponds to two C^- ions. However, in the intermediate region the Coulomb repulsion of the two C^- ions, the mutual polarization forces, and eventually the formation of the chemical bond become decisive and we can only speculate on where or even if the other potential energy curves in Fig. 3 are crossed. Nevertheless, we expect the dotted curve in Fig. 3 to be broadly correct.

At this point let us comment on the relative energies of the neutral C_2 molecule and the C_2^{2-} resonance state. These states are close in energy and presently we cannot draw a final conclusion. If C_2^{2-} is lower in energy than C_2, the dianionic resonance state cannot be observed in the electron impact detachment cross section (EIDCS). But even if the two-electron escape channel is open, the resonance will be close to threshold where the EIDCS is small [9]. (In fact, the EIDCS has been reported to be virtually zero up to an energy of about 7 eV.) Thus, in order to observe the C_2^{2-} resonance state, on the one hand, the electron scattering cross section of C_2^- could be measured. On the other hand, the C_2^{2-} resonance state should be visible in the electron impact excitation cross section, e.g., as the process

$$e + C_2^-(^2\Sigma_g^+) \rightarrow \{C_2^{2-}\} \rightarrow e + C_2^-(^2\Pi_u),$$

where $C_2^-(^2\Pi_u)$ is detected.

Metastable dianions open a new chapter in electron scattering, since based on the rare-gas-like electronic structure one may expect open channels to several bound

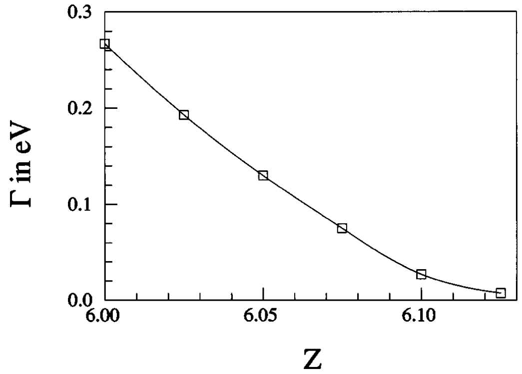

FIG. 2. Z dependence of the resonance width Γ. The data have been obtained using a partitioned one-particle basis set, where the compact part comprised 21 orbitals.

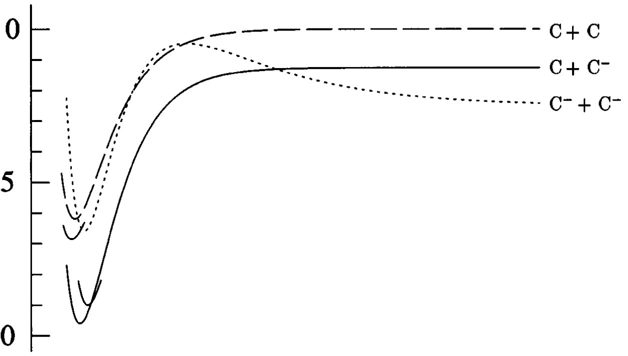

FIG. 3. Schematic representation of the relevant potential energy curves. The well depths of the three C_2^- (continuous line) and the $^1\Sigma_g^+$ C_2 state (dashed line) have been taken from the literature. The dotted curve represents the investigated C_2^{2-} state. The energy unit is eV.

monoanionic states as well as the possibility of open two-electron escape channels. Thus, in general, a competition between different autodetachment mechanisms will arise and different threshold laws could be probed. In particular, a two-electron autodetachment process has to occur simultaneously (a remaining monoanion is expected to be bound) and does not obey a Wannier law, since the remaining species is neutral. Furthermore, for molecular systems the energy gap between dianion, anions, and neutral will depend strongly on the nuclear coordinates (Fig. 3). Thus, the nuclear dynamics will have a pronounced effect on the cross sections.

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