8806 *J. Phys. Chem. A* **2000,** *104,* 8806−8813

Lifetimes of Metastable Dianions: CN_2^{2-}, C_4^{2-}, and CO_3^{2-}

Thomas Sommerfeld[†]

Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

Received: May 11, 2000; In Final Form: July 5, 2000

Almost all small dianions known from condensed phases are unstable with respect to electron loss in the gas phase. Here we study the electron autodetachment lifetimes of CN_2^{2-}, C_4^{2-}, and CO_3^{2-} employing the complex absorbing potential method as well as a new variant of the stabilization technique. The investigated temporary species show rare-gas-like closed-shell electronic ground states, and we discuss conceptional and technical differences between closed-shell resonances and typical "temporary anions" associated with electron scattering from closed-shell targets. The computed lifetimes set a lower limit for the time scales of experiments intended to observe the free dianionic systems, and the trends of the lifetimes can be understood in terms of the ideas established to rationalize the electronic stability of bound dianions. Finally, we discuss the question of which properties of metastable dianions can be extracted from bound state calculations, effectively ignoring the temporary character of the examined system.

1. Introduction

Small dianions, such as O^{2-}, C_2^{2-}, or CO_3^{2-}, are common in salts and solution chemistry, but virtually all small textbook dianions are unstable in the gas phase (see, e.g., the review articles[1−5]). The instability of these and other free dianions has been emphasised for a long time,[6−11] but only very little is known about the associated lifetimes or decay rates. While *atomic* dianions and in particular the existence of a H^{2-} resonance state attracted considerable attention (see, e.g., refs 12−15, so far C_2^{2-} is the only *molecular* dianion whose autoionization lifetime has been investigated.[16,17]

In this article we focus on small molecular dianions which are unstable with respect to vertical electron detachment. These systems correspond to resonance or temporary states and are characterized by their resonance energy or resonance position E_r and by their width Γ, which is proportional to the inverse of the lifetime $\tau = \hbar/\Gamma$. Both resonance parameters, E_r and Γ, are needed to compare different metastable states, but the width is of particular relevance, since it determines in what kind of experiment the temporary species can be observed. Specifically we study the resonance energies of the three dianions CN_2^{2-}, C_4^{2-}, and CO_3^{2-} and investigate the trends of the autodetachment lifetimes with respect to molecular structure and size.

Another important question in this context pertains to the results obtained from bound state methods. Loosely speaking, we are going to ask what information can we obtain, if we ignore the metastable character of a dianion and perform a standard quantum chemistry calculation? Standard bound state calculations have been used to investigate metastable dianions in a variety of contexts. In the first place, studies devoted to finding small stable dianions yield also geometries and energies of unstable species.[4] In the second place, many multiply charged anions have been investigated as members of an isoelectronic series (see, e.g., refs 8 and 18−20, and in the third place, there are numerous studies in the literature which compare computed energies of unstable dianions (and monoanions) without considering that the investigated species are electronically unstable. Despite the inability of bound state calculations to account for a fundamental property of the investigated temporary species, one should not underestimate their predictive power. Nonetheless, one needs to know which type of data can be extracted from a bound state calculation and how reliable these results are.

Computing lifetimes of metastable states is in general far more involved than calculations for bound systems of similar type or size, and in comparison with the highly developed quantum chemistry technology available today, there are still neither standard techniques nor generally accessible program packages for the investigation of resonances. Moreover, owing to their closed-shell electronic configuration, the temporary dianions considered here represent a new type of metastable state, where, e.g., the familiar static-exchange approach cannot directly be applied.[17] In section 2 we give a brief introduction into the investigation of free dianions[2,9] and describe the computation of the lifetime of temporary anions. In particular, the complex absorbing potential method[17,21,22] is briefly reviewed, a new variant of the stabilization method[23] is introduced, and the construction of appropriate wave functions for closed-shell resonance states is discussed in some depth. In section 3 numerical results for the three metastable dianions C_4^{2-}, CN_2^{2-}, and $CO_3^{2-}$are presented, and in section 4 our main conclusions are discussed.

2. General Considerations

This article combines the study of dianionic systems and temporary anions, two fields that had so far little overlap. In the following some background information from both fields is given, before we turn to dianionic closed-shell resonance states.

2.1. Gas Phase Dianions. Over the past decade much work has been dedicated to find the "smallest" gas phase dianion.[2] Currently, the smallest known dianions which exhibit lifetimes sufficient for mass spectrometric detection ($\tau > 10^{-5}$ s) are the AX_3^{2-} systems where A is an alkaline metal and X is a halogen atom.[24,25] These systems have so far escaped observation,[25,26] but very recently Middleton and Klein detected the closely

---

[†] E-mail: Thomas.Sommerfeld@urz.uni-heidelberg.de.

10.1021/jp0017590 CCC: $19.00 © 2000 American Chemical Society
Published on Web 09/01/2000

related species BeF_4^{2-} and MgF_4^{2-},[26] which had been predicted as early as 1991.[9] In addition, the pentaatomic systems BeC_4^{2-} [27,28] as well as TX_4^{2-} where T is Pd or Pt and X is Cl or Br[29] have been observed. Much shorter lifetimes have been addressed using electron scattering methods,[30,31] but the observed resonances seem to correspond to electronically excited states and have not unambiguously been identified.

Two decay channels are relevant to the existence of a *dianionic* system in the gas phase: electron autodetachment and fragmentation of the nuclear framework.[9,32] Both decay processes can be characterized as Coulomb explosions, and since in principle any combination of stability, metastability, or instability with respect to either channel is possible, one could distinguish a hierarchy of different levels of stability. However, owing to the influential role of mass spectrometry in this field, gas phase dianions are usually classified as long- or short-lived according to the mass spectrometrical time scale of roughly 10^{-5} s. For example, many small dianions which have been found to be stable with respect to vertical electron detachment, but to be only metastable with respect to adiabatic electron loss, or dissociation, or both, have been predicted to be observable in a mass spectrometer (see, e.g., refs 13, 24, and 33−37). In contrast, dianionic systems unstable to vertical autodetachment have been considered to be too short-lived for mass spectrometric detection and have been characterized as “nonexistent”.[10,11]

Whereas a positive electron detachment energy at the equilibrium geometry of the dianion is most probably a sufficient condition for a long lifetime, it is by no means necessary. In fact, $PtCl_4^{2-}$ has been found to possess despite its negative electron detachment energy a lifetime of about 0.1 s,[29] and similarly BeC_4^{2-} was found to be unstable to vertical autodetachment but is nevertheless observed mass spectrometrically.[27,28] From these examples it is clear that the central question is often not whether a specific species is stable or unstable in an absolute sense, but whether it is long- or short-lived on a given time scale. In spite of its ultimate instability, any dianion can be observed, if it decays sufficiently slowly in comparison with the experimental time scale.

2.2. Computing Lifetimes of Metastable Anions. A temporary or resonance state is a metastable state of a system which has sufficient energy to break up into two or more subsystems, and can be thought of as a discrete state that is embedded in and interacts with one or more continua.[38] Resonance states can be characterized by their energy or position E_r and by their width Γ. For temporary dianions E_r is the energy above the associated monoanion, that is, the energy above the target in an electron scattering experiment, and Γ is related to the lifetime $\tau = \hbar/\Gamma$. Position and width of temporary mono- or dianions can of course be extracted from the corresponding electron scattering cross section, but they can also be obtained *directly* in an approach that goes back to the treatment of the radioactive decay of nuclei by Gamow[39] and Siegert.[40] In this method resonance states are described by Siegert wave functions with complex eigenenergies

$$E_{\mathrm{res}} = E_{\mathrm{r}} - \mathrm{i}\frac{\Gamma}{2} \tag{1}$$

where E_r and Γ are the resonance parameters described above. The complex resonance energy E_{res} can be computed using complex Hamiltonian techniques of which the complex scaling (CS) method[41−43] is probably the most widely known.[44] Here we will employ, on the one hand, a complex absorbing potential (CAP)[21,45] which is similar in spirit but far easier to use in conjunction with standard bound state programs[22] and has successfully been applied to metastable states of anions[17,22] as well as cations.[46] On the other hand, we will make use of the stabilization method[23] which is “intermediate” between the direct methods (CAP and CS) and the computation of the scattering cross section. In the following paragraphs we briefly describe both techniques.

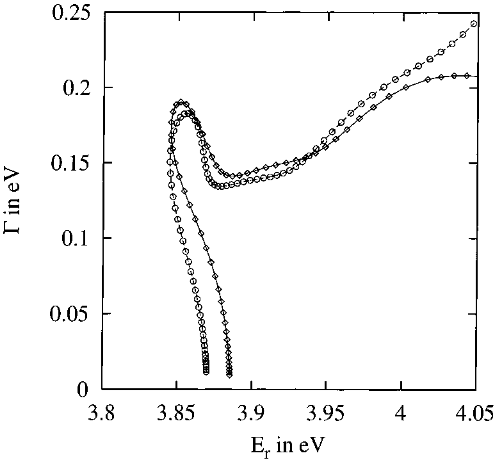

Figure 1. η trajectories for the CN_2^{2-} closed-shell resonance state. The compact AO basis sets are the TZVP (diamonds) and 6-311G* (circles) sets. η runs from 10^{-5} to 0.1 in exponentially growing steps.

The CAP method provides a simple and efficient way to study resonances using bound state techniques and has been described in detail in refs 21 and 22. One works with a parametrized non-Hermitian complex-symmetric Hamilton operator

$$H_\eta = H - \mathrm{i}\eta W \tag{2}$$

where H is the physical Hamiltonian, W is typically a real potential such as $|\mathbf{r}|^n$, and η is its strength parameter. Here we have employed two different CAP forms, a spherical quartic CAP

$$W^{(4)}(\mathbf{r}) = \mathbf{r}^4 \tag{3}$$

as well as the quadratic box-CAP suggested by Santra[46]

$$W^{(2)}(\mathbf{r};\mathbf{c}) = \sum_{i=1}^{3} W_i(r_i;c_i) \tag{4a}$$

$$W_i(r_i;c_i) = \begin{cases} 0, & |r_i| \le c_i \\ (|r_i| - c_i)^2, & |r_i| > c_i \end{cases} \tag{4b}$$

where the constants c_i define the size of the CAP box. Loosely speaking, a CAP is added to the Hamiltonian to absorb the outgoing electron, and in the complete basis set limit E_{res} does not depend on W. In the framework of a finite basis set E_{res} will to a certain extend depend on W and one typically uses complex stabilization techniques,[21] that is, one studies the η-trajectories of the complex eigenvalues $E_i(\eta)$ and a resonance is identified by a pronounced minimum of the “velocity”

$$v_i(\eta) = |\eta \frac{\mathrm{d}E_i}{\mathrm{d}\eta}| \tag{5}$$

of the corresponding trajectory (see, e.g., ref 21 or Figure 1).

The idea of the stabilization method is to place the system of interest in a box of variable size.[23] The continuum is thereby discretized, and since the resonance is more localized than the pseudocontinuum states, its energy depends far less on the box size than the pseudocontinuum energies. Thus, in a plot of the system-in-a-box energies versus box size there will be a series

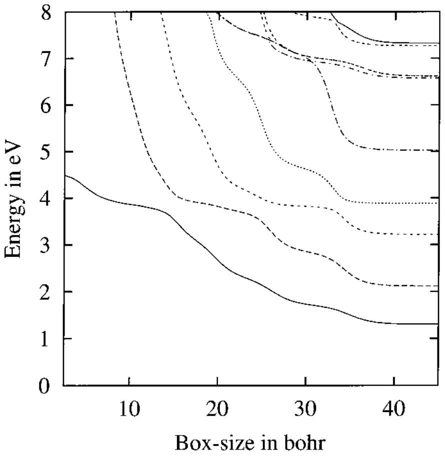

Figure 2. Stabilization plot for the CN_2^{2-} closed-shell resonance state. The compact AO basis is the TZVP basis and the box size L has been varied from 2.5 to 45.0 bohr in steps of 0.5 bohr, where the parameters c_i defining the box potential (see eqs 4 and 6 are set to L orthogonal and to $L + R$(CN) parallel to the molecular axis.

of avoided crossings, and the resonance position can be determined "by eye" from this so-called stabilization graph (see, e.g., ref 47 or Figure 2). It is more difficult to extract the width from the stabilization graph. Various schemes based on analytical continuations have been proposed (see ref 48 and references cited therein), but a more robust technique is the calculation of the resonant cross section or of the phase shift, which is then fitted to a Breit–Wigner form or its derivative, respectively.[47,49]

Variants of the stabilization method differ mostly in the way the concept of the "box" is implemented.[23,48,50] If grid methods are used, the box and its size L are obviously defined by the grid, and the box is enlarged by adding more grid points. In contrast, the definition of an appropriate "box" is not straightforward in the context of Gaussian basis sets and standard ab initio packages normally used to study temporary anions. The most popular approach consists of defining a "box" by the spatial confinement of the Gaussian basis set itself, and the box size is controlled by scaling the exponents of the diffuse functions (see ref 48 and references cited therein). Alternatively, one can add a boxlike potential to the Hamiltonian.[50] For example, the potential provided by a discretized Watson sphere[6] has been employed as a Coulomb-like box,[51] and an inverse tangent potential has been applied as a "soft" box of finite depth.[52]

Here we implement the idea of stabilization employing the boxlike potential $W^{(2)}$ defined in eq 4. The real potential $W^{(2)}$ is added to the physical Hamiltonian H

$$H(L) = H + W^{(2)}(L) \tag{6}$$

where the box size L is controlled via the parameters c_i, and in this way we obtain a "soft" box of infinite depth. In contrast to scaling variants, one has to compute the matrix elements of the Hamiltonian only once, and for each new box size L only the integrals of the one-particle operator $W^{(2)}$ have to be evaluated. In addition, we avoid problems of near-linear dependencies frequently encountered, if the exponents of the diffuse functions are scaled.

The CAP as well as the stabilization method can in principle be combined with any quantum chemical technique. However, for both the CAP and the stabilization method it is necessary to compute repeatedly several or even many eigenvalues of a Hamilton matrix that depends on an external parameter (CAP strength or box size). Thus, techniques which aim at the optimal description of just one state are in general unsuitable, and one needs a method that allows a balanced representation of several states. Here we will employ configuration interaction (CI) wave functions which have in conjunction with the CAP method been studied in refs 17 and 22.

2.3. Temporary Dianions. In this section we wish to emphasize the differences between typical "temporary anions" and closed-shell resonance states of dianions. In the literature the term "temporary anion" has mostly been used to refer to resonance states in low-energy electron scattering from neutral closed-shell targets (see. e.g., ref 53), and here we will use it in exactly this sense. Consider first a typical temporary anion. In this case the target (M electrons) exhibits a closed-shell electronic ground state; there is—usually—only one relevant target state, and a first-order resonance wave function can be written in terms of antisymmetrized (target)$^M\phi^1$ configurations where (target)^M represents the target self consistent field (SCF) configuration and ϕ is a virtual target orbital of appropriate symmetry. This is the so-called static-exchange (SE) level, a well-defined approximation which is in many respects equivalent to Koopmans' theorem (KT) approximation[54] for positive electron affinities (i.e., the extra electron is bound) and provides a starting point for higher theoretical levels including electron correlation effects.

For the dianions studied here the situation is "reversed", since the resonance state (N electrons) exhibits a closed-shell rare-gas-like electron configuration, whereas the anionic decay products show open-shell ground states which can be described in terms of a one-hole configuration. Owing to its one-hole electron configuration, the anionic target possesses usually several low-lying excited states, and the dianion can frequently decay into several channels.[17] A theoretical description of a dianionic resonance should hence be based on an SCF wave function for the closed-shell N electron state, which is however, due to its temporary character in general unavailable. In a calculation without CAP employing a suitably diffuse basis set, the resonance state will mix with pseudocontinuum states and there will be pseudocontinuum states below the resonance. It is therefore by no means clear on what kind of state an SCF calculation will converge. Thus, in contrast to temporary anions, the choice of an appropriate molecular orbital (MO) basis set for a closed-shell resonance state is a problematic step.

Here we follow an approach based on the empirical observation that small basis sets can to some extent mimic an environment in which the dianion is stable.[4,6,55] In a first step, the large basis set needed to represent the continuum in a CAP, CS, or stabilization calculation is partitioned into a compact part, which is in most cases just one of the many standard basis sets, and a diffuse part. In the language of the stabilization method, using just the compact basis set is equivalent to placing the dianion in a very small box. The lowest discretized continuum state will therefore be much higher in energy than the resonance state, and an SCF calculation will converge on the desired state. The SCF wave function obtained in this way is of course only a poor approximation of the resonance, since the artificial potential provided by the compact basis set is strong, and the occupied orbitals as well as the associated value of the negative electron detachment energies will depend strongly on the particular basis set. Nevertheless, these orbitals provide a zero-order description which actually seems to be sufficient to compute properties such as equilibrium geometries or vibrational frequencies.[4]

The SCF MOs obtained with the compact basis are then projected onto the complete basis set; that is, the compact MOs $\phi_i^{(c)}$ remain unchanged (all diffuse components are set to zero) and the new diffuse MOs $\phi_i^{(d)}$ are orthogonalized to the $\phi_i^{(c)}$. We refer to the complete set of orbitals $\phi_i^{(c)}$ and $\phi_i^{(d)}$ as projected MOs (p-MOs). Using the p-MOs we can write a CI single (CIS) wave function for the resonance taking into account the closed-shell configuration (resonance)^N and all possible single excitations (resonance)$^{N-1}\phi_i^{(c)}$ and (resonance)$^{N-1}\phi_i^{(d)}$. The single excitations do not only describe the interaction with the continuum in the ensuing CAP or stabilization calculation but also account for relaxation effects of the possibly too compact zero-order wave function. More elaborate wave functions would include all single and double excitations with respect to all first-order configurations (MR-SDCI).[17]

Since we are using orbitals optimized for the closed-shell resonance state, widths obtained at the CIS level of theory tend to underestimate the MR-SDCI widths—the "reverse" of the typical behavior at the static-exchange level for temporary anions. However, it has been found that the CIS width of C_2^{2-} is closer to the corresponding MR-SDCI value than typical static-exchange values for resonances with closed-shell targets.[17] For an investigation of alternative orbital types see ref 17.

The CIS wave function based on SCF orbitals from a smaller compact basis set is clearly not as "natural" as the KT description of ionization or electron attachment, or the SE wave function of resonances with closed-shell target states, since it involves the ambiguous subdivision of the one-particle basis set. It should nevertheless—similarly to the KT and SE levels—provide a fair first-order approximation as well as a good starting point for more refined wave functions.[17] Moreover, the partitioning of the basis set allows one to draw some connections with the Feshbach projection formalism,[38,56−58] which renders our approach particularly attractive. Within the projection formalism a resonance is described as a discrete state $|d\rangle$ that is embedded in a continuum. Due to the interaction with this continuum the discrete state acquires a width and its energy is shifted. Specifically, the SCF configuration (resonance)^N defines the discrete state $|d\rangle$ and the projection operators $Q = |d\rangle\langle d|$ and $P = 1 - Q$. The SCF energy obtained with the compact basis set is the energy of the discrete state $E_d = E^{(SCF)}$, and thus the difference between $E^{(SCF)}$ and the resonance position E_r can be identified with the level shift Δ. Let us emphasize that we do *not* use the projector formalism to compute the level shift or the resonance width, but that the specific orbital choice allows us to rationalize our results in terms of the associated concepts even though we are performing a CAP or stabilization calculation.

3. Autoionization Rates for CN_2^{2-}, C_4^{2-}, and CO_3^{2-}

In this section we discuss numerical results for the three metastable dianions CN_2^{2-}, C_4^{2-}, and CO_3^{2-}. These systems have been investigated in the study of the bonding trends in their isoelectronic series[8,19,20] as well as in the search for small gas-phase dianions.[10,59] Essentially, it had been concluded that all three species are unstable with respect to loss of an electron, but that the trends in the solid state bond lengths and vibrational frequencies can be reproduced using compact basis sets. In the following we study the associated autodetachment lifetimes and compare the properties of the free species with the findings obtained using compact basis sets.

Let us begin with CN_2^{2-}. The compact basis is Dunning's polarized triple-ζ set[60] (TZVP) which has been augmented with a diffuse [2s2p] set on carbon and a (2s10p)/[2s8p] set on nitrogen in the CAP and stabilization calculations. The diffuse functions have even-tempered exponents (scaling factor 1.4) and have been contracted to avoid near-linear dependencies. For the following discussion of the CAP and stabilization methods the bond length has been set to 1.245 Å, which is the equilibrium bond length found in an SCF geometry optimization using the compact basis set only.

In the CAP/CIS calculations the trajectory of the resonance (Figure 1) is easily identified from its eigenvector, which is dominated by the closed-shell configuration, as well as from its stabilization behavior, since all the other trajectories run very quickly far into the complex plane. Increasing the CAP strength η from very small values, the resonance trajectory (see Figure 1) first moves away from the real axis, comes slightly back, stabilizes at $\eta \approx 0.003$, and finally runs off into the complex plane; i.e., the trajectory shows the typical behavior which has been observed for many different systems. From our CAP/CIS calculation we find a width of 0.14 eV for CN_2^{2-} in the same order of magnitude as C_2^{2-}.[17] To get an idea of the basis set dependence of this result, we have repeated the calculation using the 6-311G* basis[61] as a compact set and a [1s1p] diffuse set on carbon as well as a (1s13p)/[1s10p] diffuse set on nitrogen. As can be seen from Figure 1, the resonance width is found to be only slightly sharper with the latter basis set. Thus, our width is essentially independent of the precise choice of compact or diffuse exponents.

The stabilization plot obtained with the $W^{(2)}(L)$ potential (see eqs 4 and 6), the CIS wave function, and the TZVP basis is shown in Figure 2. The avoided crossing structure indicating the resonance is clearly visible, but in addition, this plot provides some useful information about the quality of the basis set. In the first place, the basis set covers a spatial range of roughly 35 bohr in radius. For box sizes above 35 bohr all energies are practically independent of the size parameter L indicating that all integrals of the box potential $W^{(2)}$ are negligible. This "extent" of the AO basis set clearly defines an upper bound for a meaningful box size. In the second place, the density of pseudocontinuum states is rather low. Despite the almost impractical large number of diffuse basis functions in the AO basis, there are just five $^1\Sigma_g^+$ states in the energy range up to 5 eV. Thus, there are just two avoided crossings (between states 1 and 2 at $L \approx 15$ bohr and between states 2 and 3 at $L \approx 25$ bohr) that may be used to extract the resonance parameters from the stabilization plot. The behavior of states 3 and 4 at $L \approx 35$ bohr also "looks good", but numerical analysis shows that the limited extent of the AO basis set spoils the avoid crossings structure.

There are many schemes to extract approximate resonance widths "directly" from one of the avoided crossings, and using e.g. eq 11 of ref 50 and the crossing structure at $L \approx 25$ bohr, a width of about 0.2 eV is obtained. The more robust method of computing the phase shift and fitting it to a Breit−Wigner expression as suggested in ref 49 yields a width of 0.15 eV in excellent agreement with the CAP method, as it should be. We conclude that our basis set is sufficiently flexible to accurately account for the "continuum problem" and the width is essentially independent of the method to find the Siegert energy. (Of course the width still depends of the employed CI wave function and the underlying orbitals as discussed in the previous section.)

Let us now turn to the resonance position. Since the real part of the computed Siegert energy is the total energy of the resonance, but the resonance position E_r is measured relative to the target of a scattering experiment, the energy of the CN_2^- ground state $E^{(-1)}$ is needed to compute the position of CN_2^{2-}. Let us note that $-E_r$ is often referred to as negative electron affinity (positive electron affinities indicate that the electron is bound). At the CIS level of theory for the resonance there are

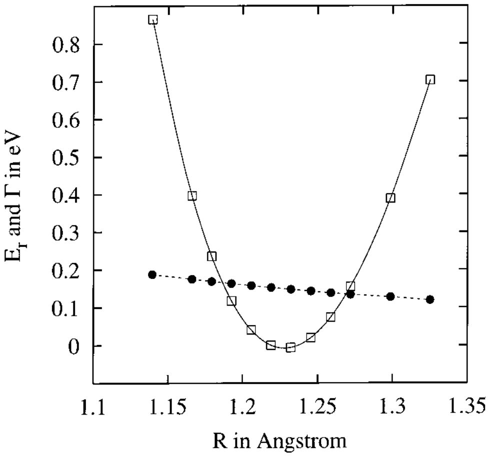

Figure 3. Complex PES of the CN_2^{2-} closed-shell resonance state. The real part E_r (open squares) has been shifted such that the minimum energy is zero. The full circles are the associated width.

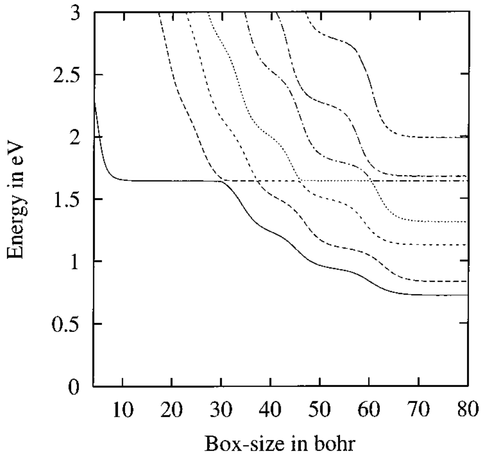

Figure 4. Stabilization plot for the C_4^{2-} closed-shell resonance state. The compact AO basis is the 6-311G* set, the outer bond length is $R_1 = 1.24$ Å, and the inner bond length is $R_2 = 1.42$ Å. The box size L has been varied from 2.5 to 80.0 bohr in steps of 0.5 bohr, where the parameters c_i defining the box potential (see eqs 4 and 6 are set to L orthogonal and to $L + R_1 + R_2/2$ parallel to the molecular axis.

basically two choices for the computation of the energy $E^{(-1)}$ of the anionic target. On the one hand, the anion ground state can be approximated at a frozen-orbital level by the corresponding one-hole configuration. In this way the internal consistency between resonance position and width is ensured, but $E^{(-1)}$ depends on the partitioning into compact and diffuse basis sets. On the other hand, a separate SCF or CIS calculation for the anion can be performed in order to include relaxation effects. These two approaches are loosely analogous to Koopmans' theorem and ΔSCF levels for electron detachment energies of bound anions.[62] For C_2^{2-} it has been found[17] that using the frozen-orbital approximation to $E^{(-1)}$ one underestimates E_r, while using $E^{(-1)}$ from a separate CIS computation one overestimates it. This observation is again similar but "reversed" to the typical behavior of temporary anions with closed-shell targets, where the resonance position is usually overestimated at the SE and underestimated at the static-exchange-plus-polarization level as compared to experimental or MR-CI results (see, e.g., ref 63).

The resonance positions of CN_2^{2-} obtained in these two ways are quite different: $E_r = 3.9$ eV using the former and $E_r = 7.3$ eV using the latter choice. Preliminary results at the MR-SDCI level point to a position of 4.6 eV, and thus, neither choice for $E^{(-1)}$ seems to be particularly balanced. Nevertheless, together the two values provide a reasonable range in which the more accurate results are found, and unless otherwise stated we will take the frozen-orbital approximation to $E^{(-1)}$ for the energy origin.

Having established a method to compute the fixed nuclei resonance energy, it is straightforward to calculate a complex potential energy surface (PES) $E_{\mathrm{res}}(\{R\})$, where $\{R\}$ represents the nuclear degrees of freedom. Whereas at the initial set of nuclear coordinates it had been necessary to carefully study the η-trajectories, at subsequent $\{R\}$ points the resonance is easily identified by its eigenvector and the optimal η-range is already known. This is a slight advantage of the CAP over the stabilization method. For CN_2^{2-} we have investigated the symmetric stretch mode and $E_{\mathrm{res}}(R)$ is shown in Figure 3, where R is the carbon−nitrogen bond length. $\Gamma(R)$ changes almost linearly and only very slowly with R, and $E_r(R)$ shows the typical potential well familiar from real PES. The equilibrium bond length $R_0 = 1.245$ Å inferred form $E_r(R)$ is almost identical with that stemming from SCF calculations using the compact basis set only. In fact, the level shift $\Delta(R) = E^{(\mathrm{SCF})}(R) - E_r(R)$ is almost constant, and for the TZVP compact basis set it has a value of 0.8 eV. Thus, the absolute energy computed with bound state methods and compact basis sets is as expected inaccurate (and very basis set dependent), but the shape of the PES is correctly represented; for CN_2^{2-} the geometrical parameters extracted from the bound state data hardly differ from those obtained from the complex PES. This behavior is unexpected, since for C_2^{2-} a significant shift in bond length had been found.[17] The decisive difference between the two systems is that for C_2^{2-} the orbitals from which electrons can autodetach (usually the (or the first few) highest occupied MO (HOMO)) is bonding whereas for CN_2^{2-} these orbitals are nonbonding in character. In other words, ignoring the metastable character of a dianion and using a bound state method with a compact basis set will yield wrong and extremely basis set dependent HOMO(s). However, if these orbitals are nonbonding in character, the shape of the PES is practically unaffected by the inadequate theoretical description, and bound state computations will yield "correct" geometrical parameters.

Based on our PES, we predict the CN_2^{2-} dianion at its equilibrium geometry to show a resonance position of roughly 4.6 eV and a width of 0.14 eV, which translates to a lifetime of approximately 5 fs. Thus, in going from C_2^{2-} to CN_2^{2-} the autodetachment lifetime of the closed-shell resonances is only slightly increased: both systems exhibit lifetimes of a few femtoseconds.

Let us now turn to C_4^{2-}. Bound state calculations with standard basis set have shown that the closed-shell dianion possesses a $D_{\infty h}$ equilibrium geometry with a long central (R_2) and two short terminal (R_1) bonds.[20,64] For this system the 6-311G* basis set has been employed as a compact set and has been augmented with a (2s13p)/[2s10p] diffuse set in the CAP and stabilization calculations. Computationally the C_4^{2-} investigation is quite different from those for CN_2^{2-} or C_2^{2-}.[17] C_4^{2-} is found to live for roughly 2 orders of magnitude longer than the latter species, and the much sharper C_4^{2-} resonance state is far more easy to distinguish from the pseudocontinuum states. In the CAP calculations the resonance trajectory stays much closer to the real axis and its velocity is over the whole η range 2 orders of magnitude slower than those of the continuum trajectories. Moreover, the associated stabilization plot (Figure 4) shows much narrower avoided crossing structures, and the resonance position can accurately be found "by eye" without any numerical analysis. However, similar to the CN_2^{2-} stabiliza-

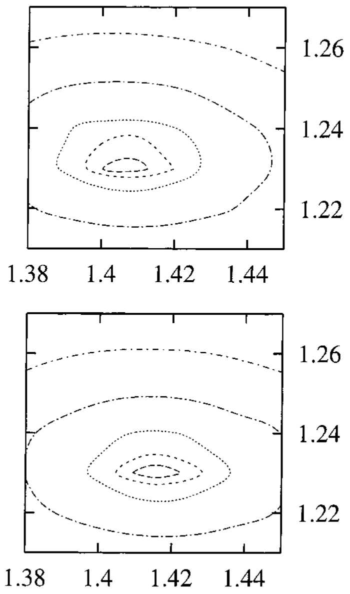

Figure 5. PES of the C_4^{2-} closed-shell resonance state. In the upper panel the real part of the complex PES $E_r(R)$ obtained at the CAP/CIS level is shown, and in the lower panel the corresponding PES computed at the SCF level using only the compact 6-311G* basis set is displayed. The inner (x-axis) and outer (y-axis) bond lengths R_2 and R_1 are given in angstroms. Both surfaces have been shifted such that the energy minimum corresponds to zero, and the contour lines correspond to 0.8, 3, 8, 30, and 80 meV. The contours are not very smooth, because the PES has been computed on a grid of 7 × 8 points only.

tion plot there is only a relatively low density of states in the relevant energy region, and one can "see" the spatial extent of the augmented basis set, which is approximately 60 bohr.

For C_4^{2-} we have computed the complex PES on a grid of 7 × 8 points in the vicinity of the SCF/compact basis set geometry assuming $D_{\infty h}$ symmetry. In the upper panel of Figure 5 E_r obtained from CAP/CIS calculation is shown, and for comparison, the PES defined by the compact basis set SCF energy $E^{(SCF)}$ is plotted in the lower panel of Figure 5. The bond length changes due to the coupling to the continuum are—similar to C_2^{2-} [17]—in the order of 0.01 Å with the shorter bond length being less sensitive. Specifically, the equilibrium geometries extracted from $E_r(R_1,R_2)$ and $E^{(SCF)}(R_1,R_2)$ are $R_1 = 1.407$, $R_2 = 1.233$ and $R_1 = 1.416$, $R_2 = 1.231$, respectively. Thus, ignoring the metastable character of C_4^{2-} leads not only to questionable total energies, but also to significant changes in the geometry which are similar in magnitude to typical electron correlation effects. In the same bond length region the associated width $\Gamma(R_1,R_2)$ is found to change smoothly between about 1 and 3 meV (Figure 6), and close to the equilibrium geometry the width is roughly 2.5 meV. We note that $\Gamma(R_1,R_2)$ is almost constant along the "symmetric stretch" coordinate $Q_S = R_1 + R_2$ and changes nearly linearly with the "antisymmetric stretch" $Q_A = R_1 - R_2$.

For the resonance position or negative electron detachment energy there are again two values depending on the approximation for the $^2\Pi_g$ C_4^- ground state. At the equilibrium geometry of C_4^{2-} we find a resonance position of 1.6 eV at the frozen-orbital level of theory, and performing a separate CIS calculation for the C_4^- ground state yields a position of 3.3 eV. As discussed above, the former and latter values for E_r are expected to under- and overestimate the position, respectively, and thus, we predict a closed-shell C_4^{2-} resonance state at roughly 2 eV above the C_4^- ground state with a lifetime of about 260 fs. In comparison with the smaller carbon cluster dianion C_2^{2-}, the C_4^{2-} resonance state is strongly stabilized: the position is decreased by about 1 eV and the lifetime is increased by roughly 2 orders of magnitude.

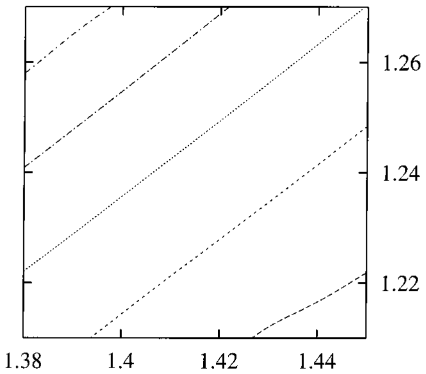

Figure 6. Width $\Gamma(R_1,R_2)$ of the C_4^{2-} closed-shell resonance state. The inner (x-axis) and outer (y-axis) bond lengths R_2 and R_1 are given in angstroms, and beginning from the lower right the contour lines correspond to 1, 1.5, 2, 2.5, and 3 meV.

The third dianion we have studied is the carbonate ion CO_3^{2-}. The carbonate ion has been investigated in the framework of isoelectronic D_{3h} symmetrical AB_3 systems,[19] and it is one of the standard examples for dianions that are well-known from solids and solutions but nevertheless unstable with respect to autodetachment in the gas phase.[10] From size and excess charge distribution arguments one may expect that its autodetachment lifetime is longer than those of CN_2^{2-} or C_4^{2-}, and thus, out of the three investigated systems CO_3^{2-} is the one most closely related to electronically stable dianions. Since we are using theoretical methods closely related to standard bound state techniques, we expected the carbonate ion to be a particular easy case for our methods. However, surprisingly, from a computational point of view the CO_3^{2-} dianion turned out to be the most difficult species.

For CO_3^{2-} we used as compact basis sets Dunning's TZVP as well as the 6-311G* set, and the p-type functions of both basis sets have been partly uncontracted in some calculations. The compact basis sets have been augmented with various sets of diffuse basis functions (even scaling factors between 1.4 and 1.8) containing up to 13 contracted p-type functions at the oxygen atoms. With any of our basis sets, even with those containing just four diffuse functions, it is straightforward to identify the resonance state, and there is no doubt that CO_3^{2-} represents a sharp resonance. The stabilization plots show sharp forbidden crossing structures, and in the CAP calculations the trajectory of the state dominated by the closed-shell configuration is by several orders of magnitude slower than those of the pseudocontinuum states. Even from the CAP calculations the resonance position can easily be extracted "by eye", since the real part of the resonance trajectory is essentially constant. At a carbon−oxygen bond length of $R = 1.3$ Å, which is close to the SCF/6-311G* optimized geometry ($R = 1.282$), the resonance position is found to be $E_r = 1.3$ eV at the frozen-orbital level and $E_r = 3.8$ eV at the CIS level for the CO_3^- anion. Moreover, calculations for different bond lengths show that similar to CN_2^{2-} the level shift $\Delta(R) = E^{(SCF)}(R) - E_r(R)$ is practically independent of R, and for the compact 6-311G* set we find $\Delta = 1.65$ eV. Consequently, the metastable character of CO_3^{2-} has virtually no influence on the geometrical data, and the PES obtained with bound state techniques and compact basis sets has the correct shape.

In contrast to the resonance position, it is very hard to obtain a reliable width from the CAP or the stabilization methods. In the CAP calculations the velocity of the resonance trajectory is much smaller than those of the pseudocontinuum trajectories; however, the stabilization behavior is weak in the sense that $v(\eta)$ has a relatively broad and shallow minimum. Moreover, the width depends substantially on the diffuse basis set and the employed CAP. These dependencies are very small in absolute terms, since all CAP/basis set combinations yield widths between 0.5 and 0.1 meV and larger basis set lead consistently to smaller widths, but the relative errors are large. In the stabilization calculations the situation is similar. The phase shift computed from an L range containing only one forbidden crossing structure can perfectly be fitted to a Breit−Wigner form, but, the different forbidden crossings yield different widths. For example, using the 6-311G* compact set augmented with a [1s13p] set of diffuse functions at the oxygen centers leads to a stabilization plot with eight forbidden crossing structures, which yield widths between 0.3 and 0.02 meV.

The computational problems in the CAP and stabilization calculations are of course not due to the methods themselves, but are due to the inflexibility of the underlying AO basis sets. The interaction of the resonance with the continuum is obviously in the same order of magnitude as the error caused by representing the Hamiltonian in a finite basis set. Loosely speaking, the width is so small that is almost vanishes in the basis set background noise. It is moreover very difficult to construct even larger atom-centered Gaussian basis sets due to increasing numerical difficulties with near-linear dependencies. From our results using a variety of different basis sets we predict the CO_3^{2-} closed-shell resonance state to possess at the CIS level of theory a width of roughly 0.1 meV. This value might still be too large by a factor of 4, but we are confident that it exhibits the correct order of magnitude. In order to compute a more accurate width for CO_3^{2-} or to investigate even longer lived autodetaching species, such as SO_4^{2-}, the quality of the basis sets needs to be improved. Possible improvements include the optimization of the contraction coefficients of the diffuse functions for each specific case, or augmenting the basis set with new types of functions, however, at the cost of sacrificing the intimate relationship with bound state techniques.

4. Discussion and Conclusions

We have studied the lifetimes of the three small dianions CN_2^{2-}, C_4^{2-}, and CO_3^{2-}, which are familiar from condensed phases but had been found to be unstable in the gas phase. These species decay by electron autodetachment and represent closed-shell resonance states. The associated autodetachment widths have been computed employing the CAP method as well as a new variant of the stabilization method in conjunction with CIS wave functions. This level of theory is comparable in quality to the SE picture for temporary anions with closed-shell targets and to the KT approximation for electron detachment energies of bound states. Our results show that the calculated width are essentially independent of the employed "continuum" method provided that the underlying AO basis set is sufficiently flexible, and for the investigated species neither the CAP nor the stabilization techniques have any decisive advantages. In contrast, the "sufficient flexibility" of the AO basis is rather crucial. In particular the width of the CO_3^{2-} dianion is very small, and it is difficult to obtain accurate results using an atom-centered Gaussian basis set.

At the CIS level we find for the three dianions CN_2^{2-}, C_4^{2-}, and CO_3^{2-} widths of 140, 2.5, and 0.1 meV, respectively, which translate into respective lifetimes of 5, 260, and 6500 fs. Moreover, using the frozen-orbital approximation for the anionic targets, the resonance positions of the three metastable dianions are 3.9, 1.6, and 1.3 eV, respectively. Let us again note that the CIS level of theory for metatstable states is roughly comparable to the ΔSCF level for bound anions, and that the values for both resonance position and widths are expected to underestimate the true values somewhat. Nevertheless, we expect the quality of our results to be better than typical SE values for temporary anions with closed-shell targets.

Our computed lifetimes set limits to the time scale of any experiment intended to observe one of the investigated dianions in the gas phase. Obviously, all three species are by more than 7 orders of magnitude too short-lived to be observable in a mass spectrometer ($\tau > 10^{-5}$ s), and only scattering techniques seem appropriate to detect CN_2^{2-}. However, C_4^{2-} and especially CO_3^{2-} live sufficiently long for the experimental techniques developed in femtochemistry.[65] Moreover, there are many systems in the lifetime range between CO_3^{2-} and 10^{-5} s, such as SO_4^{2-} or C_6^{2-}, whose lifetimes are probably much longer than that of CO_3^{2-}, but still too short for mass spectrometry (the smallest detected carbon cluster is C_7^{2-} [66,67] and only the cluster $[SO_4^{2-}(H_2O)_4]$ has been observed.[68] We hope our work will stimulate the experimental search for these and other temporary dianions.

Let us now discuss the dependence of the autodetachment lifetimes on molecular structure and size. For comparison we include the closed-shell C_2^{2-} resonance, which shows a lifetime of 3 fs at the CIS level, and its frozen-orbital position is $E_r = 2.5$ eV.[17] As a first guess one might expect that the lifetime of metastable dianions should essentially depend on the size of the system, since the spatial extent of the molecular system defines the minimal repulsion of the two excess electrons localized at opposing ends of the molecular framework. However, our results clearly show that sheer size is by far not the most relevant property, but that the lifetimes depend strongly on the particular molecular system. In our examples, the largest increase in size occurs in going from C_2^{2-} to CN_2^{2-}, but both systems have lifetimes in the same order of magnitude. Moreover, CO_3^{2-} and C_4^{2-} have the same number of atoms, and owing to its linear geometry C_4^{2-} allows the two excess charges to localize at a possibly larger distance. Yet CO_3^{2-} lives for more than 1 order of magnitude longer than C_4^{2-}.

The lifetime trends of the discussed species can be understood in terms of the concepts employed to explain the stability of certain families of bound dianions, where the key issue concerns electron-accommodating atoms or groups of atoms. All small gas-phase dianions have at least two electron-accommodating units, and depending on the structural properties and variabilities of the different systems, there is a tradeoff between compact forms possessing many electron-affine substructures and chain-like forms showing only two electron-accommodating groups but maximizing their distance (see, e.g., refs 2, 35, 37, and 69). In C_2^{2-} the extra electrons are of course distributed over the two terminal atoms, and the same is true for CN_2^{2-}, since the nonbonding HOMO has a node on the central carbon atom. Thus, in both dianions the excess electrons have to be accommodated on single, not particular electron-affine atoms, and the lifetime is correspondingly short. In C_4^{2-} there are also only two electron-accommodating groups, but a terminal C_2 unit shows a much higher electron affinity than a single carbon atom, and the lifetime of C_4^{2-} is therefore much longer. Finally, in CO_3^{2-} the excess charge can be distributed over three equivalent oxygen centers, giving rise to an even smaller autodetachment rate. The outstanding stabilities of the LiF_3^{2-} dianion[24] and the

D_{3h} symmetrical C_7^{2-} cluster[67] find thus their counterpart in the long lifetime of CO_3^{2-}.

Finally, let us summarize what information can be extracted from bound state calculations for metastable dianions employing compact basis sets. In the first place, a bound state calculation is of course necessary to conclude that a given dianion is unstable with respect to electron autodetachment. The obtained energy will however depend strongly on the finite basis set and can be loosely related to the energy needed to add one extra electron to the anion within the spatial confinement defined by the specific basis set. The corresponding negative detachment energies can nonetheless provide a useful measure for relative instabilities, if similar species are investigated with identical basis sets. However, unless the basis set dependence of the energy is studied, that is, effectively a stabilization calculation is performed, the computed energies cannot be compared to positive electron detachment energies and should be used with great care.

In contrast to the energies, geometrical parameters of metastable dianions can be computed using bound state methods. Here we need to distinguish two cases. If, on the one hand, the highest occupied MOs from which electrons can autodetach are nonbonding in character, the artifical confinement of the compact basis set has very little influence on the geometries. For example, for CN_2^{2-} and CO_3^{2-}, the shape of the PES obtained from bound state methods is practically equivalent to the real part of the complex PES from a CAP or stabilization calculation. If, on the other hand, the temporarily bound electrons occupy bonding orbitals, these orbitals need to be described correctly, and only methods that correctly incorporate the decay process will yield accurate geometries. For example, for C_2^{2-} and C_4^{2-} the differences in bond length due to the coupling to the continuum are similar in magnitude to typical electron correlation effects, and the continuum and correlation errors may add to each other.[17]

Acknowledgment. Helpful and stimulating discussions with F. Tarantelli, L. S. Cederbaum, and A. Dreuw are gratefully acknowledged. This work was supported by the Fonds der chemischen Industrie and the Deutsche Forschungsgemeinschaft.

References and Notes

(1) Kalcher, J.; Sax, A. F. *Chem. Rev.* **1994**, *94*, 2291.
(2) Scheller, M. K.; Compton, R. N.; Cederbaum, L. S. *Science* **1995**, *270*, 1160.
(3) Compton, R. N. In *Negative Ions*; Esaulov, V., Ed.; Cambridge University Press: Cambridge, UK, 1995.
(4) Boldyrev, A. I.; Gutowski, M.; Simons, J. *Acc. Chem. Res.* **1996**, *29*, 497.
(5) Wang, L.-S.; Wang, X. B. *J. Phys. Chem. A* **2000**, *104*, 1978.
(6) Watson, R. E. *Phys. Rev.* **1958**, *111*, 1108.
(7) Herrick, D. R.; Stillinger, F. H. *J. Chem. Phys.* **1975**, *62*, 4360.
(8) Pyykkö, P.; Zhao, Y. *J. Phys. Chem.* **1990**, *94*, 7753.
(9) Weikert, H. G.; Cederbaum, L. S.; Tarantelli, F.; Boldyrev, A. I. *Z. Phys. D: At., Mol. Clusters* **1991**, *18*, 229.
(10) Janoschek, R. *Z. Anorg. Allg. Chem.* **1992**, *616*, 101.
(11) Boldyrev, A. I.; Simons, J. *J. Phys. Chem.* **1994**, *98*, 2298.
(12) Robicheaux, F.; Wood, R. P.; Greene, C. H. *Phys. Rev. A* **1994**, *49*, 1866.
(13) Sommerfeld, T.; Riss, U. V.; Meyer, H.-D.; Cederbaum, L. S. *Phys. Rev. Lett.* **1996**, *77*, 470.
(14) Morishita, T.; Lin, C. D.; Bao, C. G. *Phys. Rev. Lett.* **1998**, *80*, 464.
(15) Bylicki, M.; Nicolaides, C. A. *J. Phys. B* **1998**, *31*, L685.
(16) Sommerfeld, T.; Riss, U. V.; Meyer, H.-D.; Cederbaum, L. S. *Phys. Rev. Lett.* **1997**, *79*, 1237.
(17) Sommerfeld, T.; Tarantelli, F.; Meyer, H.-D.; Cederbaum, L. S. *J. Chem. Phys.* **2000**, *112*, 6635.
(18) Pyykkö, P. *Mol. Phys.* **1991**, *67*, 871.
(19) Hotokka, M.; Pyykkö, P. *Chem. Phys. Lett.* **1989**, *157*, 415.
(20) Pyykkö, P.; Runeberg, N. *THEOCHEM* **1991**, *80*, 269.
(21) Riss, U. V.; Meyer, H.-D. *J. Phys. B* **1993**, *26*, 4503.
(22) Sommerfeld, T.; Riss, U. V.; Meyer, H.-D.; Cederbaum, L. S.; Engels, B.; Suter, H. U. *J. Phys. B* **1998**, *31*, 4107.
(23) Hazi, A. U.; Taylor, H. S. *Phys. Rev. A* **1970**, *1*, 1109.
(24) Scheller, M. K.; Cederbaum, L. S. *J. Phys. B* **1992**, *25*, 2257.
(25) Sommerfeld, T.; Child, M. S. *J. Chem. Phys.* **1999**, *110*, 5670.
(26) Middleton, R.; Klein, J. *Phys. Rev. A* **1999**, *60*, 3515.
(27) Klein, J.; Middleton, R. *Nucl. Instrum. Methods B* **1999**, *159*, 8.
(28) Dreuw, A.; Cederbaum, L. S. *J. Chem. Phys.* **2000**, *112*, 7400.
(29) Wang, X. B.; Wang, L.-S. *Phys. Rev. Lett.* **1999**, *83*, 3402.
(30) Andersen, L. H.; Hvelplund, P.; Kella, D.; Mokler, P.; Pedersen, H. B.; Schmidt, H. T.; Vejby-Christensen, L. *J. Phys. B* **1996**, *29*, L643.
(31) Pedersen, H. B.; Djuric, N.; Kella, D.; Schmidt, H. T.; Safvan, C. P.; Vejby-Christensen, L.; Andersen, L. H. *Phys. Rev. A* **1999**, *60*, 2882.
(32) Ewig, C. S.; Wazer, J. R. V. *J. Am. Chem. Soc.* **1990**, *112*, 109.
(33) Hendrickx, M.; Ceulemans, M.; Vanquickenborne, L. G. *J. Phys. Chem.* **1994**, *98*, 1117.
(34) Gutowski, G. L.; Boldyrev, A. I.; Ortiz, J. V.; Simons, J. *J. Am. Chem. Soc.* **1994**, *116*, 9262.
(35) Sommerfeld, T.; Scheller, M. K.; Cederbaum, L. S. *J. Phys. Chem.* **1994**, *98*, 8914.
(36) McKee, M. L. *J. Phys. Chem.* **1996**, *100*, 3473.
(37) Dreuw, A.; Sommerfeld, T.; Cederbaum, L. S. *J. Chem. Phys.* **1998**, *109*, 2727.
(38) Weisskopf, V. *Ann. Phys. (Leipzig)* **1931**, *9*, 23.
(39) Gamow, G. *Z. Phys.* **1928**, *51*, 204.
(40) Siegert, A. J. F. *Phys. Rev.* **1939**, *56*, 750.
(41) Aguilar, J.; Combes, J. M. *Commun. Math. Phys.* **1971**, *22*, 269.
(42) Balslev, E.; Combes, J. M. *Commun. Math. Phys.* **1971**, *22*, 280.
(43) Simon, B. *Commun. Math. Phys.* **1972**, *27*, 1.
(44) Moiseyev, N. *Phys. Rep.* **1998**, *302*, 211.
(45) Jolicard, G.; Austin, E. J. *Chem. Phys. Lett.* **1985**, *121*, 106.
(46) Santra, R.; Cederbaum, L. S.; Meyer, H.-D. *Chem. Phys. Lett.* **1999**, *303*, 413.
(47) Mandelshtam, V. A.; Ravuri, T. R.; Taylor, H. S. *Phys. Rev. Lett.* **1993**, *70*, 1932.
(48) Garcia-Sucre, M.; Lefebvre, R. *Chem. Phys. Lett.* **1986**, *130*, 240.
(49) Ryaboy, V.; Moiseyev, N.; Mandelshtam, V. A.; Taylor, H. S. *J. Chem. Phys.* **1994**, *101*, 5677.
(50) Maier, C. H.; Cederbaum, L. S.; Domcke, W. *J. Phys. B* **1980**, *70*, L119.
(51) Chao, J. S.-Y.; Falcetta, M. F.; Jordan, K. D. *J. Chem. Phys.* **1990**, *93*, 1125.
(52) Weyh, D.; Meyer, W. In preparation.
(53) Jordan, K. D.; Burrow, P. D. *Chem. Rev.* **1987**, *87*, 557.
(54) Koopmans, T. *Physika* **1933**, *1*, 1.
(55) Fowler, P. W.; Madden, P. A. *J. Phys. Chem.* **1985**, *89*, 2581.
(56) Feshbach, H. *Ann. Phys. (N.Y.)* **1958**, *5*, 357.
(57) Fano, U. *Phys. Rev.* **1961**, *124*, 1866.
(58) Feshbach, H. *Ann. Phys. (N.Y.)* **1962**, *19*, 287.
(59) Boldyrev, A. I.; Simons, J. *J. Chem. Phys.* **1992**, *97*, 2826.
(60) Dunning, Jr., T. H. *J. Chem. Phys.* **1971**, *55*, 716.
(61) Clark, T.; Chandrasekhar, J.; Schleyer, R. *J. Comput. Chem.* **1983**, *4*, 294.
(62) Kalcher, J. *R. Soc. Chem. Annu. Rep., Sect. C* **1997**, *93*.
(63) Sarpal, B. K.; Pfingst, K.; Nestmann, B. M.; Peyerimhoff, S. D. *J. Phys. B* **1996**, *29*, 857.
(64) Watts, J. D.; Bartlett, R. J. *J. Chem. Phys.* **1992**, *97*, 3445.
(65) Zewail, A. H. *Femtochemistry—Ultrafast dynamics of the chemical bond*; World Scientific: Singapore, 1994.
(66) Schauer, S. N.; Williams, P.; Compton, R. N. *Phys. Rev. Lett.* **1990**, *65*, 625.
(67) Sommerfeld, T.; Scheller, M. K.; Cederbaum, L. S. *Chem. Phys. Lett.* **1993**, *209*, 216.
(68) Blades, A. T.; Kebarle, P. *J. Am. Chem. Soc.* **1994**, *116*, 10761.
(69) Berghof, V.; Sommerfeld, T.; Cederbaum, L. S. *J. Phys. Chem.* **1998**, *102*, 5100.