Ultracold Trapped Molecules: Novel Systems for Tests of the Time-Independence of the Electron-to-Proton Mass Ratio

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Abstract. The vibrational and rotational transition frequencies in molecules are functions of the electron-to-nucleon mass ratio. They can therefore be used for experiments searching for a time-dependence of the electron-to-proton and nucleon-to-nucleon mass ratios. We propose to to perform such tests with very high precision using ultracold molecular ions trapped in a radio-frequency trap and sympathetically cooled by atomic ions. The current status of an experiment using Be^+-ions as a coolant medium to cool light diatomic molecular ions is described. An interesting perspective is to perform high-precision spectroscopy on single ultracold molecules. We sketch an approach towards this goal.

1 Introduction

A large experimental effort is currently under way to test the foundation of metric theories of gravity, the Einstein Equivalence Principle (EP) [1]. This effort is motivated in part by the difficulties in unifying the theory of gravity with quantum theory. The EP includes the principle of Local Position Invariance, which states that the fundamental constants of nature, such as the fine structure constant α, the mass ratios of the elementary particles, etc. are independent of time and position.

Tests of the time-independence of the fundamental constants can be performed by laboratory experiments or astronomical observations [2]. In laboratory tests, the frequencies of dissimilar types of oscillators are compared as a function of time, while in astronomical tests, the frequencies of the electromagnetic waves emitted in the far past by oscillators located in distant sources are compared with the current frequency values of the *same* type of oscillators as obtained in the laboratory. Table 1 gives an overview of some microscopic and macroscopic systems that define transition or oscillation frequencies.

Analysis of astronomical observations claims a variation of α on the order of 5 ppm over billions of years [7]. This claim provides increased stimulus for laboratory experiments. These have entered a new era, where use is made of the development of atomic clocks based on ultracold atoms and atomic ions, and new methods of precise comparison of optical and microwave frequencies. An improvement by more than an order of magnitude in the most stringent laboratory limits has already been achieved.

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Table 1. Dependence of the transition energy or cavity photon energy (in units of the Rydberg energy E_R) of various oscillators on fundamental constants. For the function F, see [3]. The function $G(\alpha)$ is a relativistic correction factor for principal transitions; it reduces to unity in the non-relativistic limit (small-Z atoms) [4]. The dependencies for molecular vibrational and rotational transitions are given for diatomic molecules, where μ is the reduced mass. For vibrational transitions between low-lying levels $H(m_e/\mu) \simeq \sqrt{m_e/\mu}$. The resonance frequency of a cavity is proportional to the size and thus to the interatomic spacing, resulting in $h\nu \propto E_R/\alpha$. Here, propagation of the electromagnetic wave in vacuum is assumed. For the case of monolithic cavities, see [5]. The last entry refers to the weak interaction-induced splitting between molecular levels of mirror molecules (enantiomers) [6] and to the parity non-conservation light shift in atoms. G_F is the Fermi constant, θ_W is the Weinberg angle.

Type	dependence
Hyperfine splitting	$g\,\alpha^2 F(\alpha Z)m_e/m_p$
Fine-structure splitting	α^2
Electronic transitions	$G(\alpha)$
Rotational transitions	m_e/μ
Vibrational transitions	$H(m_e/\mu)$
Cavity frequencies	α^{-1}
Parity violation splitting	G_F , $\sin^2\theta_W$

The best laboratory limits produced thus far constrain certain *combinations* of fundamental constants. For example, the recent high-precision tests concerned a comparison of hyperfine transition frequencies of ultracold atoms that yielded a test of the time-independence of $g_{Cs}/g_{Rb}\,\alpha^{0.44}$ at the level of $7\cdot10^{-16}$/yr [8]. A comparison of an optical transition in Hg^+ and the hyperfine frequency of Cs gave a limit of $7\cdot10^{-15}$/yr for the combination $g_{Cs}\alpha^6 m_e/m_p$ [9]. Vibrational transition frequencies in room-temperature molecular gases have also been investigated: a comparison of a vibration frequency of methane (CH_4) and the hyperfine frequency of Cs has led to an upper limit on the order 10^{-12}/yr for the time dependence of the ratio [11]. A similar test using the molecule OsO_4 led to a limit $2\cdot10^{-13}$/yr [10]. Taking these two results together, the ratio of the two vibrational frequencies is found to be constant at the level of 10^{-12}/yr. This may be interpreted as a limit for the time-dependence of the ratio of the characteristic nuclear masses corresponding to the vibrational modes studied.

From astronomical observations limits for individual fundamental constants have been derived. For example, concerning α the relativistic and spin-orbit energies of various atomic ions in quasars have been compared to laboratory values [4,7]. Concerning m_e/m_p, the ratio of energy differences of ro-vibrational levels in a given electronic state of molecules in distant interstellar clouds can be compared to present-day laboratory values. Based on observation of neutral H_2 absorption lines, constancy within 40 ppm was found [12,13].

2   Molecular Tests of Constancy of Electron-to-Nucleon Mass Ratios

Laboratory tests sensitive to the electron-to-nucleon mass ratio, and insensitive to other fundamental constants to lowest order, can be performed by one of the following methods [14]:

(i) Comparison of a vibrational or rotational molecular frequency and a non-relativistic electronic transition in an atom;

(ii) Comparison of a (ro-)vibrational frequency and a rotational frequency, in the same molecule or in different molecules;

(iii) Comparison of vibrational frequencies of different transitions in the same molecule or in different molecules;

(iv) Comparison of vibrational frequencies of different molecules.

The approach (iii) is based on the fact that the interatomic molecular potential is not harmonic and therefore the energy spacing between adjacent vibrational levels is not constant. The decrease in spacing for a diatomic molecule is itself a function of m_e/μ, where μ is the reduced mass of the oscillating nuclei, and of the particular molecule.

If the comparisons are performed using hydrogen molecules (H_2, H_2^+, H_3^+), the ratio m_e/m_p is accessed directly. If an arbitrary molecule is used, the ratio m_e/μ is accessed. A limit for the time-independence of m_e/m_p can only be given under the assumption that the ratios of nuclear masses are time-independent, i.e. $\mu/m_p = const$. However, if rotational or vibrational transitions of *different* molecules are compared (approach (iv)) then the ratio of nuclear masses can be probed [15]. An example is the comparison of H_2^+ and D_2^+ or H_2^+ and HD^+. Such tests would probe the time-independence of the strong interaction [16].

Referring to Fig. 1, we can describe the approaches (ii) and (iii) by

$$\frac{d\ln\left(\frac{\nu_a - \nu_b}{\nu_a}\right)}{dt} = (1-s)\frac{d\ln(m_e/m_p)}{dt} \, , \tag{1}$$

$$\frac{d\ln\left(\frac{\nu_1}{\nu_2}\right)}{dt} = (s_1 - s_2)\frac{d\ln(m_e/m_p)}{dt} \, . \tag{2}$$

Here the coefficients s_k are defined by the derivative of the relevant transition frequencies ν_k with respect to the electron-to-proton mass ratio,

$$\frac{m_e/m_p}{\nu_k}\frac{d\nu_k}{d(m_e/m_p)} \equiv s_k. \tag{3}$$

The coefficients s_k can be calculated using quantum chemical algorithms. For example, Hilico et al. have performed such calculations for the vibrational levels of the H_2^+ and D_2^+ molecules [17].

To reach an interesting level of sensitivity and open up a direction for future progress, it is certainly necessary to use ultracold molecules. Since the approaches (i-iv) can be applied to essentially any molecule, molecular ions can
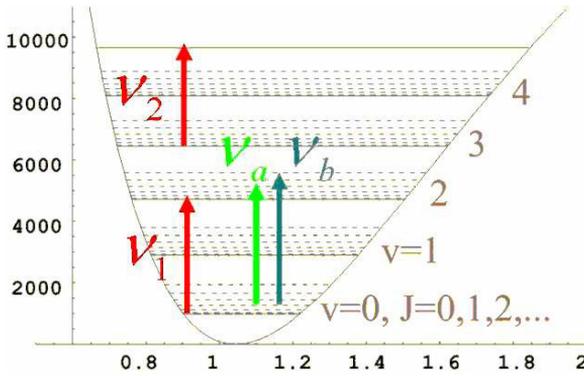
Fig. 1. Principle of the test of the time-independence of m_e/m_p. The relative difference of two ro-vibrational transition frequencies ν_a, ν_b sharing a common level (method (ii)) or the ratio of two vibrational transition frequencies ν_1, ν_2 (method (iii)) is measured over the course of time.

be considered. These are favorable, since they can be (translationally) cooled using sympathetic cooling by laser cooled atomic ions [18]. When crystallized, the molecular ions are in the Lamb-Dicke regime, and the ro-vibrational transitions will exhibit resolved sidebands. The linewidths are expected to be equal to their natural linewidth, on the order of tens of Hz for dipole-allowed vibrational transitions in the ground electronic state, and below 1 Hz for pure rotational transitions in the lowest vibrational state. The quality factors of the transitions are therefore in the range of 10^{11} or larger.

On the experimental side, laser sources for performing fundamental or overtone vibrational or stimulated Raman spectroscopy with such resolution can be implemented. For example, continuous-wave optical parametric oscillators (OPO) currently can provide radiation at wavelengths up to 4 μm with free-running linewidths below 100 kHz. Diode lasers of similar linewidth are available in the telecom wavelength range. Alternatively, difference frequency generation can be used if low power levels are sufficient. The linewidth of the sources can be reduced by frequency-stabilization to cavities. Such laser sources can be used to excite fundamental or overtone vibrational transitions.

The detection of excitation to vibrational or rotational states within the electronic ground state in cold molecular ion ensembles is not straightforward, since the number of molecules will be limited and fluorescence detection is impractical (fluorescence decay rates are small and fluorescence wavelengths lie in the mid-infrared). Destructive detection of excitation is one approach and will be described in the next section. A proposal for nondestructive detection of molecular excitation is presented in the last section.

Rotational transition frequencies can be determined from a frequency difference $\nu_a - \nu_b$ between two ro-vibrational excitations, as shown in Fig. 1, or from the frequency difference of two waves used for a stimulated Raman transition within the same vibrational state, or by direct microwave spectroscopy.

Since the frequencies of the various transitions to be compared will typically be very different (except if method (iv) is used with molecules appropriately selected to have accidental degeneracies), frequency comb techniques will have to be used.

In order to reach interesting sensitivities for time-independence, the evaluation of systematic shifts will be of central importance. The experience gained from work on cold atomic ion frequency standards will certainly be of significance.

3 Sympathetic Cooling of Molecular Ions and Spectroscopy

In our laboratory, two experiments dedicated to translational cooling of molecular ions are under way. The first experiment uses ^{9}Be$^+$ as a coolant ion, the second uses ^{137}Ba$^+$. The choice of Beryllium was made in order to be able to efficiently trap light molecular ions, in particular molecular hydrogen ions. The much heavier Barium ions can be used to trap heavier molecular ions, even proteins, provided they are sufficiently highly charged [19]. The issue here is the requirement of stable trapping, which constrains the allowed charge-to-mass ratio of the molecular ions compared to that of the coolant ions.

One of our goals in studying molecular hydrogen ions is to measure the proton and deuteron masses spectroscopically. Besides containing the most fundamental nuclei, the diatomic molecular hydrogen ions H_2^+, D_2^+, HD^+, and HT^+, being relatively simple three-body quantum systems, are also the only ones for which ab-initio theory has the potential of reaching sufficient accuracy in the near future. The Schrödinger equation for such systems can be solved with essentially arbitrary accuracy (10^{-14}) as a function of the masses of the three particles. The required relativistic and QED corrections have so far been worked out to a relative accuracy on the order of 10^{-7}, but with potential for future improvements. Precision measurements on these ions could eventually lead to highly accurate values for m_e/m_p and the nuclear mass ratios m_p/m_d as well as m_p/m_T. Among the above ions, the heteronuclear ion HD^+ is of particular interest from an experimental point of view since dipole-allowed vibrational transitions can be excited. We stress that even at the current stage of theoretical accuracy tests of the time independence of essentially any nuclear-to-electron mass ratio, as opposed to a measurement thereof, can be performed using corresponding molecular ions.

In the Be$^+$-experiment, we use a four-rod linear radio-frequency trap with end caps. The central electrode length is 16 mm, rod diameter is 9.9 mm, rod-to-trap-axis distance is 4.3 mm. The 313 nm cooling radiation is generated using doubly-resonant sum frequency generation (SFG) of a resonantly doubled Nd:YAG laser, and a Ti:Sapphire laser at 760 nm [20]. The Nd:YAG laser is frequency-stabilized to a hyperfine transition in molecular iodine; since the cavity used for SFG is locked to the Nd:YAG laser and the Ti:Sapphire laser is locked to the cavity, the sum frequency wave is then also frequency stabilized. An AOM placed before
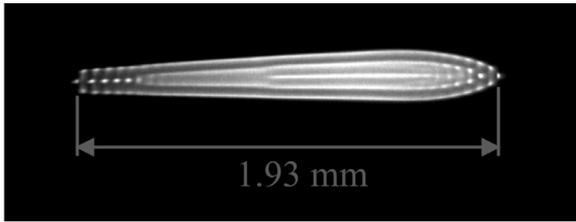
Fig. 2. Stable Beryllium Coulomb crystal. Cooling laser frequency was locked approx. 35 MHz red-detuned from resonance.
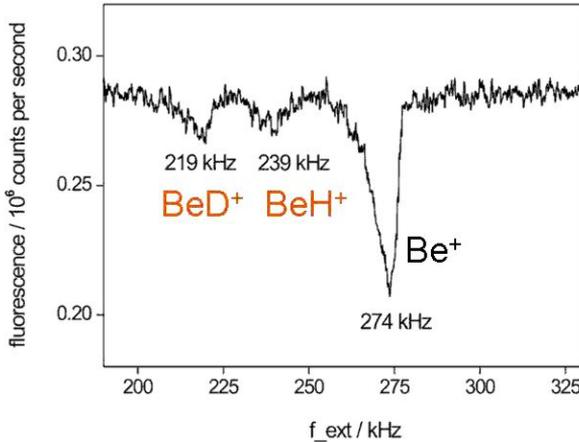
Fig. 3. Secular oscillation mass spectrum showing presence of beryllium hydride and deuteride ions produced by chemical reactions. Shown is fluorescence rate of the Be^+ ions as a function of frequency of the ac voltage applied to a 2 cm wide plate electrode at a distance 9.5 mm from the trap axis. Ac amplitude was 0.5 V.

the iodine stabilization setup allows to shift the stable UV frequency within a range of 340 MHz. UV output powers up to 80 mW were obtained.

Be$^+$-Coulomb crystals of various sizes and shapes were obtained by varying the trap and loading parameters. Figure 2 is an example of a small crystal.

We have produced molecular ions in situ by leaking HD gas into the UHV chamber for 1–2 min with pressure of $4 \cdot 10^{-10}$ mbar. Chemical reactions between HD and the crystallized Be$^+$-ions resulted in BeH$^+$ and BeD$^+$. Their presence is proven by excitation of the secular oscillation in radial direction. The excitation heats the Be$^+$ ion ensemble by Coulomb interaction and results in a decrease in Be$^+$ fluorescence. Figure 3 shows the mass spectrum of the ions contained in the trap. The secular frequencies lie within 1 % of the expected values. The crystal remains stable during excitation, but experiences a small Be$^+$ ion loss. Beryllium hydride and deuteride are heavier than the coolant ion. It is therefore expected that they are located outside the Be$^+$-crystal. Indeed, no significant dark regions are visible within the Be$^+$-crystal. We expect that the molecular
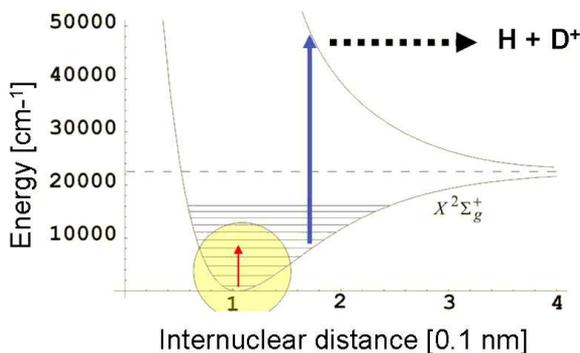
Fig. 4. Detection of molecular excitation by 1+1 REMPI. A vibrational transition can be detected since molecules in an excited vibrational state can be selectively dissociated with UV radiation of appropriate wavelength. The method is also applicable to selectively detect population in any particular rotational state of the lowest vibrational state if first a vibrational excitation laser is used to transfer population from the rotational state to an appropriate vibrational level

ions were sympathetically cooled and crystallized; to prove this statement, we would need to perform molecular spectroscopy or add another fluorescent atomic ion ensemble of greater mass so that the molecular ions would become "visible" as a dark shell between the added atomic ions and the Be^+-crystal [18].

As mentioned above, the detection of population in a long-lived ro-vibrational or rotational state poses a problem. A destructive detection method is possible by means of 1+1 resonance multi-photon ionization (REMPI). We plan to implement this for spectroscopy of HD^+, see Fig. 4.

Since for sympathetically cooled molecular ions in equilibrium with the laser-cooled atomic ions the internal temperature will at most be 300 K (the temperature of the vacuum chamber), in diatomic molecular ions only the lowest vibrational level will be populated initially. A vibrational excitation to be detected will transfer a fraction of these ions into another vibrational level. If a pure rotational transition (e.g. by stimulated Raman transition) is to be detected, it can be followed by a one-photon laser vibrational excitation to an excited vibrational level. The task then is to dissociate molecules preferentially from such an excited vibrational level. At least for HD^+ this is indeed possible, as shown in Fig. 5. A large ratio between the dissociation probabilities from a state $v' \neq 0$ and from $v = 0$ can be achieved for any v' by appropriate choice of dissociation wavelength. A good choice of target vibrational level and dissociation wavelength are $v' = 4$ (corresponding to a $0 \to 4$ transition wavelength around $1.4\,\mu m$) and 266 nm (obtainable by frequency-quadrupling a Nd:YAG laser). The required photodissociation energy densities can be obtained from pulsed or cw lasers. For the $v' = 5$ target level one might be able to use the 313 nm cooling radiation as dissociation light, if it is sufficiently intense. A suitable ion optics and ion counter to extract and detect the dissociation products is required.
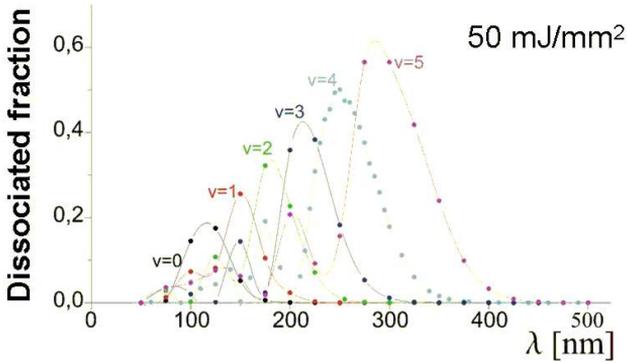
Fig. 5. Theoretical photodissociation probability of HD^+ ions in various vibrational states vs. excitation wavelength for an energy density of $50 \, mW/mm^2$ and 1 s duration. [21,22].

4   Quantum Jump Spectroscopy

Obviously, a destructive detection method is not favourable, because of the need to reload the trap and possibly the need to reestablish a sufficiently similar configuration of the molecular/atomic ion ensemble. Various types of non-destructive detection of molecular excitation can be envisaged. Here we consider one method that is of interest if one seeks to perform spectroscopy on a single molecule. This might be the ultimate goal in precision molecular spectroscopy, since the spatial state of the molecule is then well-defined, and the determination of systematic effects is simpler. The method we propose is related to the concepts of implementing quantum gates [23] and of performing high resolution spectroscopy of atomic ions that do not have laser cooling transitions [24]. Basically, an appropriate atomic ion is used as a monitor of the internal state of the test ion (here a molecule).

Figure 6 sketches a simplified view of the procedure. A single molecular ion and a single coolant atomic ion are prepared in the trap. The atomic ion level scheme must have an accessible long-lived state. This can be an electronic state connected to the ground state by a dipole-forbidden transition, or a hyperfine state in the ground electronic state [24]. Here we consider the first case for simplicity, but the latter case would be relevant if the coolant ion is Be^+. The two-ion crystal is cooled by resolved sideband cooling to the motional ground state of e.g. the axial crystal mode [25]. In our model scheme this requires the P-state linewidth to be smaller than the phonon frequency. However, in practice resolved sideband cooling would be performed on a dipole-forbidden atomic transition, so that this condition can be satisfied. Note that there is no need to focus the sideband cooling radiation selectively onto the atomic ion.

The atomic ion is then transferred to the metastable state (here a D state). Now the internal vibration of the molecule is excited, with the laser tuned to the blue motional sideband. The ion crystal motional oscillation is thereby simultaneously excited. The figure shows a fundamental vibrational excitation ($v, J =$
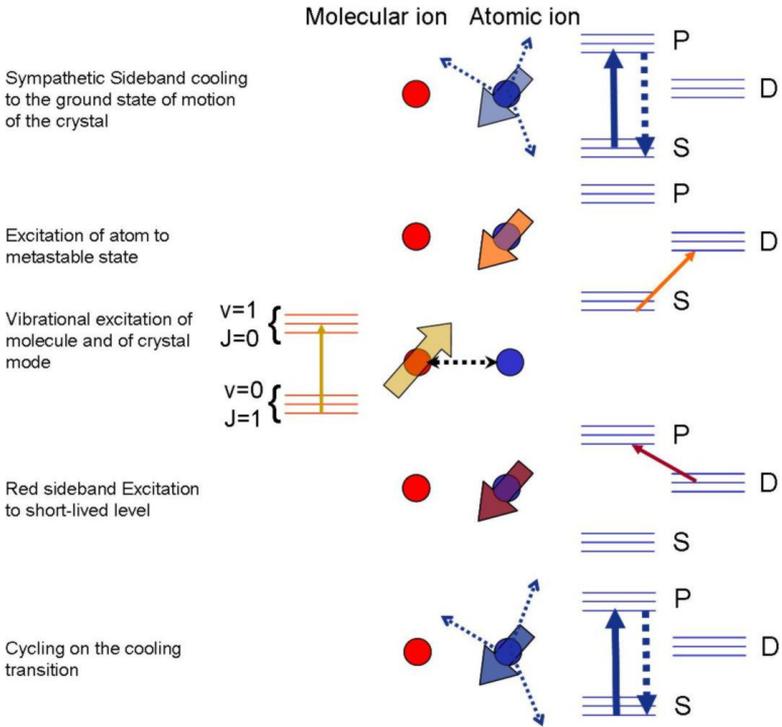
Fig. 6. Schematic of a method for detecting quantum jumps in molecules with high signal-to-noise ratio. The sublevels shown in the level diagrams of molecule (left) and atom (right) are the vibrational states of the crystal oscillation along the trap axis.

$1) \rightarrow (v+1, J=0)$ of the molecule and the excitation of one crystal phonon. The analogue can be done with a pure rotational excitation $(v, J) \rightarrow (v, J \pm 2)$ by using stimulated Raman scattering.

The next step consists in detecting whether a crystal phonon is present or not. To this end, the atomic ion is transferred to one of the levels of the cooling transition, using red-detuned light. This ensures that if no phonon is present, the atomic ion remains in the metastable state.

As a result, the atomic ion has been brought into a level from which the cycling can be driven, resulting in a high fluorescence rate. Thus, if the internal excitation of the molecule has taken place, this results in fluorescence from the atomic ion; the molecular quantum jump has thereby been detected. The fluorescence continues even when the molecule decays back into the ground state. Note that a ro-vibrational molecular transition $(v = 0, J = 1) \rightarrow (v = 1, J = 0)$ is a cycling transition, albeit one with a small decay rate, due to the small transition frequency.

For a spectroscopic measurement, the outlined procedure would be repeated for different values of the molecular excitation frequency.

This method, albeit technically difficult, would allow to perform spectroscopy on narrow molecular transitions with similar sensitivity as in the electron shelving method of single atomic ion spectroscopy.

5   Conclusion

In this paper we have pointed out that ultracold molecular ions have the potential for being used for measurements of very high spectroscopic precision, similar to what has already been demonstrated with atomic ions. Vibrational and rotational transitions limited only by the narrow natural linewidth are in principle accessible. Some approaches on how to perform the spectroscopy of molecular transitions in practice have been mentioned.

This opens up fascinating possibilities for the metrology of the electron-to-proton and proton-to-deuteron mass ratios (both absolute determination as well as time-independence tests). Measurements of parity violation, tests of the symmetrization postulate, and of the electron dipole moment in molecules are further perspectives on the use of molecular ions for fundamental physics studies. Of course, on the physical chemistry side, precision molecular structure studies will represent a huge new domain of activity, which is likely to challenge quantum chemical theory significantly.

Acknowledgments

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